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*First Summary Report
Basic Research in Thermionics*

Part I

CESIUM PERMEATION THROUGH TANTALUM

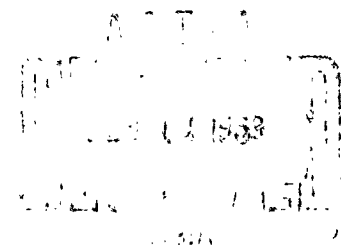
1 November 1961 to 31 October 1962

OFFICE OF NAVAL RESEARCH

Project No. 099-364

Contract Nonr 3705(00)fbm

January 1963



TEXAS INSTRUMENTS
INCORPORATED

CESIUM PERMEATION THROUGH TANTALUM

Summary Report

1 November 1962 to 31 December 1962

Prepared by: R. A. Chapman
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TEXAS INSTRUMENTS
INCORPORATED

FIRST SUMMARY REPORT
BASIC RESEARCH IN THERMIONICS
PART I:
CESIUM PERMEATION THROUGH TANTALUM

FOREWORD

This report presents a portion of the work performed under Contract Nonr 3705(00)fbm. Work on low work function semiconductor collectors is described in part II of the First Summary Report on Basic Research in Thermionics under this contract.

Major technical contributors to this work were Dr. R. A. Chapman, Mr. D. A. Peterman, Dr. G. F. Wakefield, and Dr. P. F. Woerner. About seventeen professional man-months were devoted to this subject.

This research was performed in the research laboratories of Texas Instruments Incorporated. The major portion was performed in Texas Instruments Central Research Laboratories. The last few months of the weight-loss and tracer studies were performed by Drs. Woerner and Wakefield in the Materials & Controls division of Texas Instruments. Dr. R. A. Chapman was over-all project manager for this work. Dr. P. F. Woerner was project manager for the work performed in the Materials & Controls division. The project was carried out under the auspices of the Office of Naval Research and directed by CDR John J. Connelly.

FIRST SUMMARY REPORT
BASIC RESEARCH IN THERMIONICS
PART I:
CESIUM PERMEATION THROUGH TANTALUM

TABLE OF CONTENTS

<u>Part</u>		<u>Page</u>
	SUMMARY	i
I	INTRODUCTION	1
II	THEORY AND BACKGROUND	4
	A. Permeation	4
	B. Modes of Permeation - Effect of Physical Leaks	7
	C. Diffusion in Non-Porous Solids	9
	D. Interpretation of Diffusion Experiments in Finite Slabs	13
III	EXPERIMENTS	16
	A. Permeation-Ion Current Studies	16
	1. Introduction	16
	2. Tube Design	17
	3. Processing	17
	4. Test Results	18
	5. Conclusion	21
	B. Weight-Loss Studies	31
	1. Introduction	31
	2. Experimental Work	32
	3. Data	35
	4. Discussion	41
	C. Diffusion of Radioactive Cs ¹³⁴ in Tantalum	44
	1. Introduction	44
	2. Experimental	45
	3. Experimental Results	47

TABLE OF CONTENTS
(Cont.)

<u>Part</u>	<u>Page</u>
IV. COMPATIBILITY OF RESULTS AND CONCLUSIONS.	69
A. Radioactive Tracer Experiments	69
B. Weight-Loss Experiments.	70
C. Ion-Current Experiments.	71
REFERENCES.	72

APPENDIX

DISTRIBUTION LIST

LIST OF ILLUSTRATIONS

<u>Tables</u>	<u>Page</u>
I METAL RADII.	9
II SUMMARY OF EXPERIMENTAL DETERMINATIONS	36
III DIFFUSION DATA FOR SINGLE CRYSTAL EXPERIMENTS.	50

<u>Figures</u>	<u>Page</u>
1 Diode Used in Previous Work.	22
2 External Collector Diode	23
3 Method of Breaking Cs Capsule.	24
4 Diode Under Test	25
5 I-V Curves for R3Cs.	26
6 Schematic of Measuring Circuit	27
7 Vacuum I-V Curve for Diode R5Cs.	28
8 Comparison of Emitter Surface Before and After Processing.	29
9a Grain Structure Before Processing (156 x).	30
9b Grain Structure After Processing (156 x)	30
10 Test Vessel.	33

TABLE OF CONTENTS

(Cont.)

List of Illustrations

<u>Figures</u>	<u>Page</u>
11 Sample CT 3	37
12 Samples CT 4 and CT 4B	38
13 Blank Sample	39
14 Sample CT 6	40
15 Cesium Diffusion Tube	46
16 Sample 27B. Diffusion of Cs ¹³⁴ in Single Crystal Tantalum. 1400° C, 24 Hours.	51
17 Sample 28A. Diffusion of Cs ¹³⁴ in Single Crystal Tantalum. 1400° C, 48 Hours.	52
18 Sample 26B. Diffusion of Cs ¹³⁴ in Single Crystal Tantalum. 1600° C, 24 Hours.	53
19 Sample 27A. Diffusion of Cs ¹³⁴ in Single Crystal Tantalum. 1600° C, 48 Hours.	54
20 Sample 25A. Diffusion of Cs ¹³⁴ in Single Crystal Tantalum. 1800° C, 24.8 Hours.	55
21 Sample 26A. Diffusion of Cs ¹³⁴ in Single Crystal Tantalum. 1800° C, 36 Hours.	56
22 Sample 25B. Diffusion of Cs ¹³⁴ in Single Crystal Tantalum. 1800° C, 48 Hours.	57
23 Sample 120A. Diffusion of Cs ¹³⁴ in Single Crystal Tantalum. 1800° C, 24.75 Hours.	58
24 Diffusion Coefficient as a Function of the Reciprocal Temperature	59
25 Laue X-Ray Pattern of Tantalum Prior to Diffusion Run	60
26 Laue X-Ray Pattern of Tantalum After Diffusion Run	60
27 Autoradiograph of Single Crystal Tantalum After Exposure to Cs ¹³⁴	61
28 Photomicrographs of As-Received Tantalum Sheet and the Same Material After Diffusion. 294 x, Etched.	63
29 Sample 22A. Diffusion of Cs ¹³⁴ in Polycrystalline Tantalum. 1600° C, 12 5/12 Hours.	64
30 Sample 24A. Diffusion of Cs ¹³⁴ in Polycrystalline Tantalum. 1800° C, 11 Hours.	65
31 Photograph of an Autoradiograph of Polycrystalline Tantalum. After Exposure to Cs ¹³⁴ . Note Accumulation of Activity at the Left End. Magnification 27 x.	67

FIRST SUMMARY REPORT
BASIC RESEARCH IN THERMIONICS
PART I:
CESIUM PERMEATION THROUGH TANTALUM

SUMMARY

A plasma thermionic converter concept has been proposed which uses cesium permeation through a tantalum emitter to obtain space charge neutralization of electron current from this emitter. The objective of this project was to determine if the permeation rate of cesium through tantalum was sufficiently large for feasibility of the concept. It has been shown that the concept is not feasible because the permeation rate of Cs through tantalum is too small.

Cesium permeation through tantalum has been studied in the temperature range 1400° C to 1800° C with cesium pressures up to 13 mm-Hg. This phenomenon was investigated for potential application as a hollow, ion-dispensing emitter for a plasma thermionic converter. Three methods were used in this study: (1) measurement of ion current from a hollow, polycrystalline tantalum emitter internally connected to a cesium reservoir, (2) measurement of weight-loss from a hollow, polycrystalline tantalum container with a cesium reservoir attached, with both suspended from a microbalance into a radiant furnace, and (3) direct measurement of the diffusion coefficient in single-crystal and polycrystalline tantalum utilizing radioactive Cs¹³⁴.

From this study we have found: (1) the diffusion coefficient of cesium in single crystal tantalum is $4.9 \times 10^{-10} \text{ cm}^2/\text{sec}$ at 1800° C, the diffusion activation energy is 1.06 eV and the pre-exponential factor is $2.47 \times 10^{-7} \text{ cm}^2/\text{sec}$; (2) diffusion in polycrystalline samples was irregular and strongly dependent on grain structure; (3) the weight-loss from a polycrystalline vessel with walls 0.002-in. thick depends on annealing history but is the order of $0.04 \mu\text{g}/\text{cm}^2 \cdot \text{sec}$ ($30 \mu\text{a}/\text{cm}^2$) at 1800° C with permeation activation energy

of 4.05 eV; and (4) prior observations of ion-current from hollow emitters could be attributed to physical leaks.

This study indicates that the permeation rate through a 0.010-in.-thick tantalum emitter at 1800° C is much too small to neutralize 5 amps/cm² of electron current. For single-crystal tantalum the neutralized electron current would be no higher than 0.85 ma/cm² (using tracer data and assuming a maximum cesium concentration of 0.1 at. % in tantalum) and for polycrystalline tantalum, 3.0 ma/cm² of electron current (from weight-loss data). Thus, the permeation currents are too small for practical application. This permeation could have a long-term effect, producing a cesium loss from the diode in designs having thin, hot tantalum separating the diode-interspace from vacuum (space applications).

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SECTION I

INTRODUCTION

FIRST SUMMARY REPORT
BASIC RESEARCH IN THERMIONICS
PART I:
CESIUM PERMEATION THROUGH TANTALUM

SECTION I
INTRODUCTION

The results which J.-M. Rocard obtained while at Texas Instruments and later published in enlarged form^{1,2} led to the present study. His experimental device was a thermionic converter using a hollow tantalum emitter (with an internal cesium reservoir) and a cold trap on the diode interspace plenum. After several days, he observed cesium permeation evidenced by increased contact potential difference and reverse (ion) current.

The introduction of cesium ions into the diode interspace from the interior of the emitter provides an ion source for space charge neutralization which is not dependent on cesium pressure in the diode interspace. Thus, the same ion current can be obtained for a far lower cesium pressure in the diode interspace.

The advantage of such a device would be a reduction in internal resistance of the converter by reducing electron collisions with neutral cesium atoms. This operation could be maintained in steady state by utilizing a recirculating pump to transfer liquid cesium from the cold trap (attached to the diode interspace) to the cesium reservoir attached to the hollow emitter.

In this report permeation is used as a generic term to denote transport of vapor from one reservoir through a solid wall to another, lower-pressure reservoir. It denotes no judgement as to the mechanism of transport, which could be bulk diffusion or surface diffusion along cracks. The permeability is often defined³ as the volume in STP cubic centimeters per second (or molecules per sec) per square centimeter of wall area, per millimeter of wall thickness, per centimeter of pressure differential. In this report the permeation rate in molecules per cm² per second will be used, rather than the permeability. To transform this parameter to permeability, the permeation

rate must be normalized to unit thickness and 1 cm cesium pressure. Conversion of the units of cesium permeation used in these studies are: 1 ma/cm^2 is equal to $1.33 \text{ ug/cm}^2 \text{ sec}$ is equal to $6.25 \times 10^{15} \text{ atoms/cm}^2 \text{ sec}$.

The required cesium permeation rate is that necessary to neutralize the space charge resulting from the emitted electrons. If the thermionic converter is to operate at maximum power with a 5 amp/cm^2 saturated forward electron current, an ion current of no less than $(1/500 \times 5) \text{ amps/cm}^2$ or $10 \text{ milliamps/cm}^2$ must be available. In a standard cesium thermionic converter, this ion current could be obtained at the hot emitter using cesium vapor in the interspace corresponding to a cesium reservoir temperature of 95°C , assuming 100% ionization. There must be a permeation rate of 6.25×10^{16} cesium atoms/cm² sec to obtain this ion current.

The permeation might result from bulk diffusion. In this case it would be valuable to have an order-of-magnitude estimate of the diffusion coefficient of cesium in tantalum to provide space charge neutralization. A lower limit on the necessary diffusion coefficient may be obtained using Eq. (4) (section II) and taking the largest possible estimate of maximum concentration of cesium in tantalum. The maximum concentration observed in the radioactive tracer studies described in this report was 0.01 at. %. It seems that a cesium concentration of 0.1 at. % ($5.5 \times 10^{19} \text{ atoms/cc}$) would be a good upper limit. If the thickness of the tantalum wall is $2.54 \times 10^{-2} \text{ cm}$, the diffusion coefficient must be greater than $3 \times 10^{-5} \text{ cm}^2/\text{sec}$ to obtain a 10 ma/cm^2 ion current. For the experimental devices studied, the saturated electron currents were the order of 5 ma/cm^2 . In this case a diffusion coefficient of $3 \times 10^{-8} \text{ cm}^2/\text{sec}$ would be sufficient to obtain space charge neutralization. If the actual diffusion coefficients are larger than these values, an ion rich sheath will form at the emitter, and the neutral cesium emission rate will increase.

It is also possible that small diameter ($\sim 1 \text{ micron}$) pores or grain-

boundary cracks could provide the necessary ions. This subject will be discussed further in section II of this report.

Three experimental methods were used to study the permeation of cesium through tantalum: (1) ion-current from a hollow, polycrystalline-tantalum emitter attached to an internal cesium reservoir, (2) weight-loss of a thin-walled, polycrystalline tantalum vessel (with cesium reservoir attached) suspended from a micro-balance into a radiant furnace, and (3) tracer studies of polycrystalline and single-crystal tantalum using Cs^{134} . The first two methods measure permeation rates, while the third measures the diffusion coefficient directly. Although the diffusion coefficient is extremely interesting theoretically, the permeation rate is the parameter of direct interest to application. The ion-current method is limited in that accurate measurements of the permeation rate at low voltages can be made only when the emitter is being operated in an electron-rich mode; that is, there is an electron sheath rather than an ion sheath at the emitter.

SECTION II

THEORY AND BACKGROUND

R. A. Chapman

SECTION II

THEORY AND BACKGROUND

R. A. Chapman

A. Permeation

The permeation rate of a vapor through a wall may be limited by any one of several series processes; the slowest process will determine the rate. The rate may be limited by (1) adsorption at the inner wall, (2) passage from the inner surface into the volume of the wall, (3) diffusion through the wall, (4) passage from the volume onto the outer surface, or (5) desorption from the outer surface of the wall. The ion current and weight-loss experiments measure the over-all permeation phenomena, while the radioactive tracer studies directly measure the middle process, diffusion.

To translate the permeation data into a knowledge of the diffusion coefficient, the diffusion must be proved or assumed to be the rate limiting process in transferring cesium by permeation. Cesium is thought to be adsorbed and desorbed from tantalum in ionic form, the form in which cesium is most likely to diffuse through tantalum. Furthermore, evaporation from a monolayer of cesium on tantalum above 1400° C is quite rapid, and the diffusion rate of cesium through tantalum is expected to be very slow. Therefore, the assumption that the diffusion mechanism is the rate-limiting mechanism in cesium permeation through tantalum seems warranted. In this way, the diffusion coefficient can be estimated from the permeation data.

In diffusion theory the permeation rate, p , is simply the diffusion "current" per unit area as given in Fick's law of diffusion:

$$p = - D \nabla C \quad (1)$$

where D is the diffusion coefficient in cm^2/sec and ∇C is the gradient of the diffusant concentration (C in atoms/cc).

In the present study the permeation is measured from a thin-walled, cylindrical vessel with an internal plenum of cesium vapor. Let the inside radius be a , the outside radius b , and the wall thickness, $b - a = \ell$. The measured permeation rate will be the value of p normal to the outer surface; hence,

$$p_s = -D \left(\frac{\partial c}{\partial r} \right)_{r=b}, \quad (\text{atoms/cm}^2 \text{ sec}). \quad (2)$$

The transient solutions to this equation with boundary conditions applicable to the experiments reported here can be found by transforming the solution to similar problems in heat flow.^{4,5} Using the boundary conditions

- 1) $r = a:$ $c = c_a$ for all t
- 2) $r = b:$ $c = 0$ for all t
- 3) $a < r < b:$ $c = 0$ for $t = 0$,

the solution⁵ can be found in terms of $k = b/a$:

$$p_s = -D \left(\frac{\partial c}{\partial r} \right)_{r=b} = \frac{Dc_a}{\ell} \frac{k-1}{k \ln k} \left[1 + \frac{2k^{1/2} \ln k}{k-1} \sum_{n=1}^{\infty} (-1)^n e^{-\frac{\pi^2 n^2}{\ell^2} Dt} \right]. \quad (3)$$

In the experiments reported here, k is always less than 1.2 (usually much closer to 1), in which case $\frac{k^{1/2} \ln k}{k-1}$ and $\frac{k-1}{k \ln k}$ are very close to 1.

This expression can be used to measure the diffusion coefficient directly. Since n^2 appears in the negative exponential, only the first term of

the series will be important a short time after initiation at the transient. If the vapor pressure of the internal plenum is suddenly reduced, with the wall temperature unchanged, the permeation will soon be in an exponential decay with time constant t_0 :

$$t_0 = \frac{l^2}{\pi^2 D}.$$

Thus, knowing the thickness of the wall, a measurement of t_0 gives D . If l is 0.010 inch and D is $2.9 \times 10^{-5} \text{ cm}^2/\text{sec}$ (as estimated to neutralize an electron current of 5 amps/cm^2), cesium diffusion would decay with a period of two seconds after reduction of the cesium pressure in the internal reservoir. If D is $4.9 \times 10^{-10} \text{ cm}^2/\text{sec}$, the period is roughly 37 hours. A comparable "time lag" method can be used on the integrated permeation during a start-up transient.⁶

When t becomes much larger than $\frac{l^2}{\pi^2 D}$, Eq. (3) reduces steady state,

and the measured permeation rate per cm^2 is

$$p_s = \frac{Dc_a}{l} \frac{k-1}{k \ln k} \cong \frac{Dc_a}{l}. \quad (4)$$

Now c_a is the concentration of diffusant in the wall next to and in equilibrium with the cesium vapor of the internal plenum. Thus, it is the solubility, s .

The experimental permeability, $p_s l$ at a standard pressure gradient, is generally expressed in terms of an activation energy H_p :

$$p = p_0 e^{-\frac{H_p}{kT}}.$$

The permeability can be expressed in terms of solubility and the diffusion coefficient through Eq. (4). As will be discussed later, the diffusion coefficient is also described in terms of an activation energy H_D . Assuming a similar temperature dependence for the solubility, the permeation activation energy can be decomposed.

$$p = D_0 e^{-\frac{H_D}{kT}} s_0 e^{-\frac{H_s}{kT}},$$

so that

$$H_p = H_D + H_s.$$

B. Modes of Permeation - Effect of Physical Leaks

So far, only the decomposition of the permeation activation energy into diffusion and solubility activation energies has been particular to the mechanism for transport of cesium through tantalum which will result in ions. The emitters used have been polycrystalline tantalum, so processes other than bulk diffusion through the lattice must be considered.

The ion current, weight-loss and some of the tracer studies were performed with thin polycrystalline tantalum. With very thin, polycrystalline walls there is a possibility that outgassing at high temperatures and thermal cycling may cause actual cracks to appear at large-angle grain boundaries. Since crack formation could be a gradual process, its definition must be made clear.

A fairly straightforward operational definition of a leak in a true metal can be made: if a measurable helium leak rate is observed through the cold metal, there must be a physical leak. This stems from the fact that the noble gasses do not dissolve in, or permeate true metals (at least to any measurable extent).^{7,8}

Actually, permeation of cesium through a very small crack may be advantageous. If the crack is thin enough, most of the transport of cesium will be in ionic form via surface diffusion. This process has been used to great advantage in ion propulsion with porous refractory metals⁹ as ion-emitters.

Instead of considering a crack directly, a quick understanding of the magnitudes involved can be obtained using a cylindrical pore model.

The conductance, G , of a hole through a wall can be calculated using the model of a cylindrical hole of radius a and length l for Knudsen flow at pressures less than $a p_{\mu} < 5$ microns cm.¹⁰

$$G = 30.48 \frac{a^3}{l} \left(\frac{T}{M} \right)^{1/2} \text{ liters} \cdot \text{sec}^{-1}. \quad (5)$$

In this equation T is the temperature and M the mass of the leaking gas in grams per mole.

When cesium passes through this pore, there will be both Knudsen and surface transport. The percent of transport as surface diffusion will increase, however, as the end of the pore away from the cesium reservoir is approached. In the range of parameters comparable to the case under study, the net result is that the total flow of cesium is not much larger than would be predicted on the basis of Knudsen flow alone; but for pore radii of a few microns practically all cesium leaves the far end of the tube as ions from surface adsorbed cesium dispersed onto the outer surface.⁹

Thus, some feeling for the total transport of cesium through a cylindrical pore can be obtained on the basis of Knudsen flow alone. With Eq. (5) this can be transformed into a helium leak rate.

A cesium leak through tantalum from a reservoir at 150°C must have a conductance of 0.029 cc/sec to provide 1.6 μ amps of ion current. From Eq. (5), a cylindrical pore which would provide this cesium ion current would likewise have a 0.075 cc/sec helium conductance. If the helium pressure is 1 mm Hg on the reservoir side of the tube, this helium conductance gives a leak rate of about 10^{-4} standard cc/sec. This helium leak rate is very large and is easily detected on helium leak detectors which have sensitivities of the order of 10^{-9} standard cc/sec. Thus, a pore or an array of pores which provide a cesium ion current of 1.6 μ amps could be easily detected using a helium leak detector.

A cesium Knudsen conductance of 0.029 cc/sec at 150°C with a wall thickness of 0.002 inch would require a single pore radius of 14 microns. This radius would result in a large fraction of Knudsen flow straight through the pore without ionization. A pore radius of 1 micron would yield a majority of surface conductance near the exit of the pore and near 100% ionization. It would take about 3000 such pores to give 1.6 μ amps ion current. Perhaps this would approximate a small crack.

C. Diffusion in Non-Porous Solids

A knowledge of the sizes of the diffusing atoms or ions and the crystal atoms (or lattice constant) is absolutely necessary for a proper appreciation of the magnitude of diffusion coefficients of cesium in tantalum. Table I presents the metal radii for several refractory metals and cesium. Pauling's crystal radii are given for several ionized species which might diffuse through the host refractory metal lattice. Because cesium will be ionized on the surface of the high work function metals Ta and W, and because the cesium is so much smaller than the neutral atom, diffusion of cesium through the bulk metal will certainly be dominated by the positive ion species.

Table I¹¹

<u>Species</u>	<u>Radius (Angstroms)</u>
Ta	1.43
W	1.37
Cs ⁰	2.63
Cs ⁺	1.69
Ba ⁺⁺	1.35
Na ⁺	0.95
Li ⁺	0.60
O ⁻⁻	1.40
Cu ⁺	0.96

The diffusion coefficient which is to be used in Fick's law [Eq. (1)] can usually be expressed in terms of an activation energy E_D :

$$D = D_0 e^{-\frac{E_D}{kT}},$$

where D_0 is a constant. This relation is to be expected theoretically.

In the kinetic theory of gases, the diffusion coefficient is $\frac{\lambda \bar{v}}{3}$, where λ is the mean free path and \bar{v} the average velocity of the molecule. In a lattice where the diffusant jumps from one quasi-equilibrium position to another, the diffusion coefficient can be shown to be

$$D = A \ell^2 \nu,$$

where ν is the frequency with which atoms jump out of the equilibrium position, ℓ the distance between equilibrium positions, and A a constant which depends on the diffusion mechanism and the coordination of available lattice sites (or interstices). The derivation of the frequency, ν , determines D_0 and E_D .

A rough feeling for the magnitude of D_0 can be found on a simple model of $\nu = \frac{\bar{v}}{\ell} e^{-\frac{E}{kT}}$, where \bar{v} is the mean thermal velocity of the particles. On this basis D_0 is $A \ell \bar{v}$. With ℓ the order of 3 \AA and \bar{v} the order of $3 \times 10^4 \text{ cm/sec}$, D_0 is the order of $9 \times 10^{-4} A \text{ cm}^2/\text{sec}$, where A is the order of magnitude of 1. Thus, D_0 is about $10^{-3} \text{ cm}^2/\text{sec}$. Most experimental self-diffusion D_0 's are between 10^{-1} and $10 \text{ cm}^2/\text{sec}$. Experimental chemical-diffusion D_0 's, to be discussed later, are between 10^{-9} and $10 \text{ cm}^2/\text{sec}$, a range too wide to be theoretically acceptable.

The theory of the various diffusion mechanisms has been thoroughly treated by a number of authors^{12,13,14} and will not be elaborated here. The most acceptable derivation of the frequency, ν , is from Wert and Zener¹⁵ and can be applied to the diffusion mechanisms to be considered here.

Many possible bulk diffusion mechanisms may apply to this study. Self-diffusion of the refractory metal in its own lattice is important to the

present study only in providing a comparison. Tantalum and tungsten are similar body-centered-cubic crystals. In self-diffusion in tungsten, D_0 is $11.5 \text{ cm}^2/\text{sec}$ and E_D is 3.27 eV . In tantalum between 2100 and 2800°K , D_0 is $2 \text{ cm}^2/\text{sec}$, and E_D is 4.78 eV .¹⁶ Near 1800°K , grain boundary diffusion becomes very rapid. A Russian measurement of tantalum self-diffusion near 1250°C of $2.5 \times 10^{-13} \text{ cm}^2/\text{sec}$ must include grain boundary diffusion.¹⁷ Self-diffusion in bcc crystals has been interpreted as resulting from a 4-ring interchange mechanism but is probably not active in Ta and W. The interest of the present study, however, concerns chemical diffusion; that is, the study of diffusion of chemical impurities in a host lattice.

When impurity concentrations in chemical diffusion become high, the activation energy E_D and D_0 become concentration-dependent. In the present case of cesium diffusion through tantalum, low concentrations are expected, and concentration dependence of E_D and D_0 will not be considered.

The most rapid chemical diffusion process is interstitial diffusion, if it is allowed. In this mode the impurity atom travels through the host lattice via the interstices between host atoms of the crystal lattice. In bcc crystals such as tungsten and tantalum there are two types of interstices with different void-radii: tetrahedral interstices with a radius of $0.291 R$, and octahedral with a radius of $0.154 R$, where R is the radius of the coordinating metal atoms. Thus, the larger tetrahedral voids have radii of 0.417 and 0.400 \AA for Ta and W, respectively. Clearly, cesium ions cannot occupy the interstices even with extreme distortion of the lattice, and diffusion of 1.69 \AA radii cesium ions cannot proceed by means of the interstices in Ta or W.

Thus, the only chemical-diffusion mechanisms which need be considered are those in which the cesium ions travel substitutionally in the tantalum host lattice. Very often, low activation energies are found in chemical diffusion. The "solute atom-vacancy" model of Johnson¹⁸ has been invoked to

describe this phenomenon. In this model, vacancies are most easily formed near the substitutional atom. The impurity and vacancy subsequently diffuse together as a "molecule" through the lattice.

Unfortunately, the low experimental activation energies are usually accompanied by D_0 's several orders of magnitude below the acceptable range. It has been suggested that this anomaly is experimental and is caused by grain boundary diffusion^{12,13} or a concentration dependence of D_0 .

Studies of the diffusion on silver¹⁹ and zinc²⁰ in face-centered-cubic copper have shown that grain boundary diffusion along low-angle grain boundaries is no larger than the crystal lattice. When the tilt angle becomes larger than 20° , however, greatly enhanced diffusion is observed in a direction parallel to the dislocations and equal to lattice diffusion normal to the dislocations. These results are taken to imply that there is no enhanced diffusion (with silver and zinc in copper, at least) associated with single, well-separated dislocations.¹²

Silver (1.44 \AA) is also larger in radius than the host copper (1.28 \AA) lattice if it is in the same charge state as copper, as would be expected since both are Group I-b elements. The analogy to cesium in tantalum is not complete, however, since tantalum is a bcc and copper a fcc metal.

In addition to diffusion along a grain boundary, there will also be diffusion laterally out of the boundary into the grains. Experimental measurements of diffusing impurities are taken by measuring the total concentration at a particular depth from the surface of the sample. Fisher²¹ has analyzed the interpretation of such experiments in terms of a simplified model. His analysis leads to a value of $\frac{D_l}{D_{gb}^{\delta}}$, where D_l is the lattice diffusion

coefficient, D_{gb} the diffusion coefficient along the grain boundary, and δ a thickness typical of the grain boundary width. This quantity is obtained from the variation of the logarithm to the base 10 of the diffusing concentration, C , with depth y :

$$\frac{d \log_{10} C}{dy} = - \frac{2^{1/2}}{2.3} \left(\frac{D_{gb}}{D \delta} \right)^{1/2} \left(\frac{1}{\pi D t} \right)^{1/4},$$

where t is the diffusing time.

In diffusion of cesium through tantalum there is the additional effect of oxygen which may be in the tantalum bulk and "condensed" at the grain boundaries. It is common to outgas tantalum at temperatures in excess of 2000°C. However, it has been found²² that it is necessary to outgas at 2600 to 2800°C in a vacuum of less than 5×10^{-6} mm Hg to obtain complete oxygen-outgassing of tantalum.

The presence of oxygen raises the possibility that cesium could leach out the oxygen at grain boundaries and/or in some way speed up the diffusion of cesium.

Thus, interstitial diffusion of cesium in tantalum is a priori ruled out, there are several possible substitutional diffusion mechanisms, and data exist on several similar chemical diffusion systems.

D. Interpretation of Diffusion Experiments in Finite Slabs

Experiments which are designed to approximate a half-finite solid in cartesian co-ordinates (solid fills half-plane for $x \geq 0$) are most easily interpreted analytically. In this case the diffusion current is in only one direction, from the single wall. The solution of the diffusion equation in this geometry is a complementary error function under the following boundary conditions: the concentration is initially zero throughout the solid, and the concentration at the boundary is brought to a value, C_0 , and kept at this value for times $t \geq 0$. If the concentration is sampled in small laps, the

concentration per lap will be given by the derivative of the error function, yielding a Gaussian function. This analysis has been used in the present work and is discussed in section III-C.

The foregoing analysis would approximate the radioactive tracer experiments well if the sample were lapped in total to a very small fraction of the sample thickness. Because in some cases the samples were lapped a significant fraction of their half-thickness, the conditions under which the diffusion from the other wall becomes significant must be examined.

The experimental results would be most completely described by a model using a slab of thickness l , an initial zero concentration throughout the slab, and a concentration C_0 at $x = l/2$ and $x = +l/2$ for all times $t \geq 0$. This can be obtained by transforming the solution to a corresponding thermal conduction problem⁴ by substituting the diffusion coefficient D for the thermal conductivity κ . The concentration is given by

$$C = C_0 + \frac{4C_0}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} e^{-\frac{D(2n+1)^2 \pi^2 t}{l^2}} \sin \left\{ \frac{(2n+1) \pi x}{l} \right\}. \quad (6)$$

The derivative of this solution which will give the concentration per lap for small laps is

$$\begin{aligned} \frac{\Delta C}{\Delta x} &= \frac{4C_0}{l} \sum_{n=0}^{\infty} e^{-\frac{D(2n+1)^2 \pi^2 t}{l^2}} \cos \left\{ \frac{(2n+1) \pi x}{l} \right\} \\ &= \frac{2C_0}{l} D_2 \left(\frac{x}{l}, i \frac{4\pi D t}{l^2} \right), \end{aligned}$$

where D_2 is the second theta function.²³ This can be transformed to a relation involving the one-boundary solution, $\left(\frac{\Delta C}{\Delta x} \right)_0$, times the zero theta function:

$$\frac{\Delta C}{\Delta x} = \left(\frac{\Delta C}{\Delta x} \right)_0 D_0 \left(-\frac{ix\ell}{4\pi Dt}, \frac{i\ell^2}{4\pi Dt} \right)$$

$$= \frac{C_0}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \left[1 + \sum_{n=1}^{\infty} (-1)^n \left\{ e^{-\frac{n^2 \ell^2}{4Dt} \left(1 - \frac{2x}{n\ell}\right)} - e^{-\frac{n^2 \ell^2}{4Dt} \left(1 + \frac{2x}{n\ell}\right)} \right\} \right].$$

Thus, as long as $\ell^2 \left(1 - \frac{2x}{\ell}\right) \gg 4Dt$, the solution is nearly the same as the half-infinite plane solution. In the experiment reported in section III-C, the largest $4Dt$ is $3 \times 10^{-4} \text{ cm}^2$ compared to a ℓ^2 of $(0.020 \text{ inches})^2$ or $2.58 \times 10^{-3} \text{ cm}^2$. This indicates that the sample can be lapped 32.5% of its total thickness with an error less than 5% (in $\frac{\Delta C}{\Delta x}$) through use of the half-infinite solid assumption. For a 0.020-inch thick sample this would be 208 microns ($x^2 = 27 \times 10^3 \text{ microns}$). Therefore, the analysis utilizing Gaussian functions in section III-C is quite sufficient.

SECTION III
EXPERIMENTS

PART A
PERMEATION-ION CURRENT STUDIES

D. A. Peterman
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SECTION III

PART A

PERMEATION-ION CURRENT STUDIES

D. A. Peterman

1. Introduction

This report describes the measurement of cesium permeation through solid tantalum at high temperature by one particular method: ion current measurements from a cesium-vapor-filled, hollow tantalum emitter in a plasma diode-like structure. Results of previous experiments indicated significantly large permeation rates through tantalum.^{1,2} The present study was initiated to study the permeation process as thoroughly as possible by ion current measurements.

A typical test diode used in the previous tests is shown in Fig. 1. Most of these tests were made using a tantalum tubular emitter and a cesium reservoir. The emitter was made from a 0.062-inch-diameter Ta tube with a 0.010-inch wall. A section of the tube about 1.25 inches long was machined down to a 0.002-inch wall in the region to be used as an emitter.

Ion current measurements which correspond to large permeation rates were observed in the diodes. Open circuit voltages increased from less than 1 Volt to more than 3 Volts because cesium coated the collector. Equilibrium was reached in three to four days for tantalum emitters with cesium reservoirs. These tubes were thoroughly He leak checked after assembly but could not be checked during or after testing. Although large permeation rates were observed, the transport mechanism could not be determined from the initial results.

During this study it was decided that the previous measurements did not rule out a Cs leak which developed during operation as an explanation for the observed results. Since He is most often used for detecting very small leaks, the test diodes were modified to permit He leak checks after outgassing and again after testing. Although the He atom is smaller than the Cs atom, a large He leak would indicate appreciable Cs leakage also.

2. Tube Design

The original design (Fig. 1) was prone to failure and difficult to fabricate. A new design to eliminate these difficulties and permit more accurate measurements was used for all testing on this contract. One of these tubes is shown in Fig. 2. The basic advantages of this design are (1) an external collector for accurate temperature control and measurement, (2) elimination of practically all electrical leakage between emitter and collector, (3) an all-metal reservoir with a copper pinch-off seal to eliminate failures caused by cesium attack on glass-metal seals, (4) a guard ring geometry collector which allows more accurate current measurements by eliminating end effects, and (5) a nickel guide to hold the emitter in proper alignment during the tests while allowing for thermal expansion.

Cesium was introduced by breaking a glass capsule sealed in a metal reservoir. Although breaking the capsules with the diode on the vacuum system was a problem at first, this problem was solved by pinching the reservoir tube where a 0.025-inch tungsten wire had been wound around an annular scratch on the cesium capsule (Fig. 3). Thus, the force from the clamp was concentrated on a scratch around the glass tube, considerably reducing the force required.

3. Processing

The diodes were mounted on the vacuum system with the reservoir connected by an auxiliary tubulation to the vacuum system (see Fig. 2). This was necessary to obtain a high vacuum in the reservoir also. The system was

baked at 350°C for 24 hours or more; then the filament was outgassed at 2100-2200°K for at least 24 hours. The final pressure was always below 10^{-8} mm Hg.

For the first diode (R3Cs) the reservoir was sealed off after outgassing, and the diode was sealed off from the vacuum system for testing. The other diodes were left on the vacuum system so helium leak checks could be made. The vacuum system with a diode under test is shown in Fig. 4.

4. Test Results

a. Tube R3Cs

The first diode (R3Cs) was tested under the following conditions: 1900°K emitter temperature, 200°C collector temperature and 150°C Cs reservoir temperature. The measured ion current increased slowly with time to a steady value of about 0.5 ma/cm^2 in about four days. The open circuit voltage of the diode increased from an initial value of 0.5 Volt to 3.6 Volts in two days. The short circuit current went from 0.01 ma/cm^2 (vacuum value) to 2.3 ma/cm^2 in four days. Some data are shown in Fig. 5. Applying a liquid N_2 cold trap did not significantly affect the measured ion current. The diode failed after 11 days of testing because of a crack at the glass seal-off of the Cs reservoir. This was believed to be caused by Cs attack on the glass because the seal had been at room temperature for 36 hours prior to failure. These results were similar to those of the previous work but still did not determine the cause of the large cesium permeation rates.

b. Tube R4Cs

To determine if a leak occurs in the emitter after the diodes are sealed onto the vacuum system, the second diode (R4Cs) was built with two He capsules in the reservoir with the Cs capsule. After processing (baking and outgassing), the reservoir was sealed off and a He leak detector was connected to the vacuum system (i.e., emitter-collector space). One of the He capsules was then broken to test for a leak in the emitter. The leak

detector immediately indicated a large leak. The diode was sealed off from the vacuum system and tested under the same conditions as R3Cs. The results from R4Cs were identical to those of R3Cs except for a slightly faster rise time (10-12 hours compared to 20-24 hours for R3Cs).

Ion current measurement was found to be accurate if proper care was taken to eliminate such errors as secondary emission, electron current from emitter, leakage across glass surfaces as a result of Cs films, and photo-emission from the collector.

A liquid N_2 cold trap was applied to the 8 mm tube used to connect the diode to the vacuum system, as was previously done with R3Cs. As before, no change was observed in the ion current, even after four to six hours. The same result was observed with the reservoir heater off and the diode operating normally (i.e., from Cs in the emitter-collector space). The pressure difference could, at most, equal the Cs vapor pressure in the diode, about 10^{-6} mm Hg (room temperature). The rate of Cs accumulation in the cold trap was therefore limited to the arrival rate at the opening of the 8 mm tube. The area of the opening is 0.28 cm^2 . The arrival rate at 27°C is about 10^{14} atoms/sec. The leakage rate of Cs from the reservoir can be estimated from the He leak rate, which was at least the order of 1 cc/sec at 1 mm Hg. The corresponding Cs leak rate at 150°C reservoir temperature is at least 2×10^{14} atoms/sec. This shows that applying a cold trap to the diode after a week of operation would not remove the accumulated Cs from the diode quickly enough for a change in ion current to be observed in a matter of hours. A large percentage of the accumulated Cs would have to be removed before the pressure would be reduced below the room temperature value. Therefore, the collector and outside walls of the diode must be kept at a constant (low) temperature so the ion current due to arrival rate from the emitter-collector space can be calculated and subtracted from the observed ion current to yield the true permeation rate. This conclusion was substantiated by testing in a dry ice-acetone bath.

c. Tube R5Cs

This tube was processed as usual. A guard ring geometry collector was used which consisted of three Kovar rings separated by 7052 glass seals (see Fig. 2). Thus, current measurements could be made essentially without end effects when the two outer rings were held at the same potential as the center (or measuring) ring. A schematic diagram of the measuring circuit is shown in Fig. 6. This system permitted continuous variation in the diode potential except for very small negative voltages where the vacuum output was insufficient to buck the minimum battery voltage (1.5 V dc). A typical vacuum I-V curve is shown in Fig. 7. The tube was broken when the He leak check was attempted after the reservoir was sealed off from the vacuum system. This failure resulted from the difficulty in breaking the glass He capsule inside the copper reservoir tube with the diode still on the glass vacuum system. This problem was solved by the method described on page 17 (see Fig. 3).

d. Tube R6Cs

After processing, vacuum data were taken to establish the diode characteristics. The collector was of the guard ring design used on R5Cs. The leak check of the emitter was again positive. The size of the leak was of the same order as observed with R4Cs. To ascertain the cause of the leak, the tube was carefully taken apart and examined under a microscope. Figures 8 and 9 show metallographic pictures of the emitter. Figure 8 is a comparison (10 x) of the emitter surface appearance before and after processing. Figure 9 shows a comparison (156 x) of the grain size before and after processing. The large grain growth is apparently caused by recrystallization which occurs when the emitter is outgassed above the recrystallization temperature (1200°C). The emitter was put on the He leak detector and the leak was localized to an area about 1/4-inch long near one end of the reduced section. No cracks or holes could be observed on the surface of the emitter in this region.

5. Conclusion

The observed diode characteristics did not differ significantly from the results of other plasma diode studies and will not be analyzed here.

The most significant result of these studies was the discovery that the tantalum tubing used as an emitter could not be processed without a leak occurring between the emitter reservoir and the emitter-collector space. Therefore, prior observations of ion-current from hollow emitter could be attributed to physical leaks. Further work in this area was discontinued in favor of other methods for studying cesium permeation.



Fig. 1 Diode Used in Previous Work

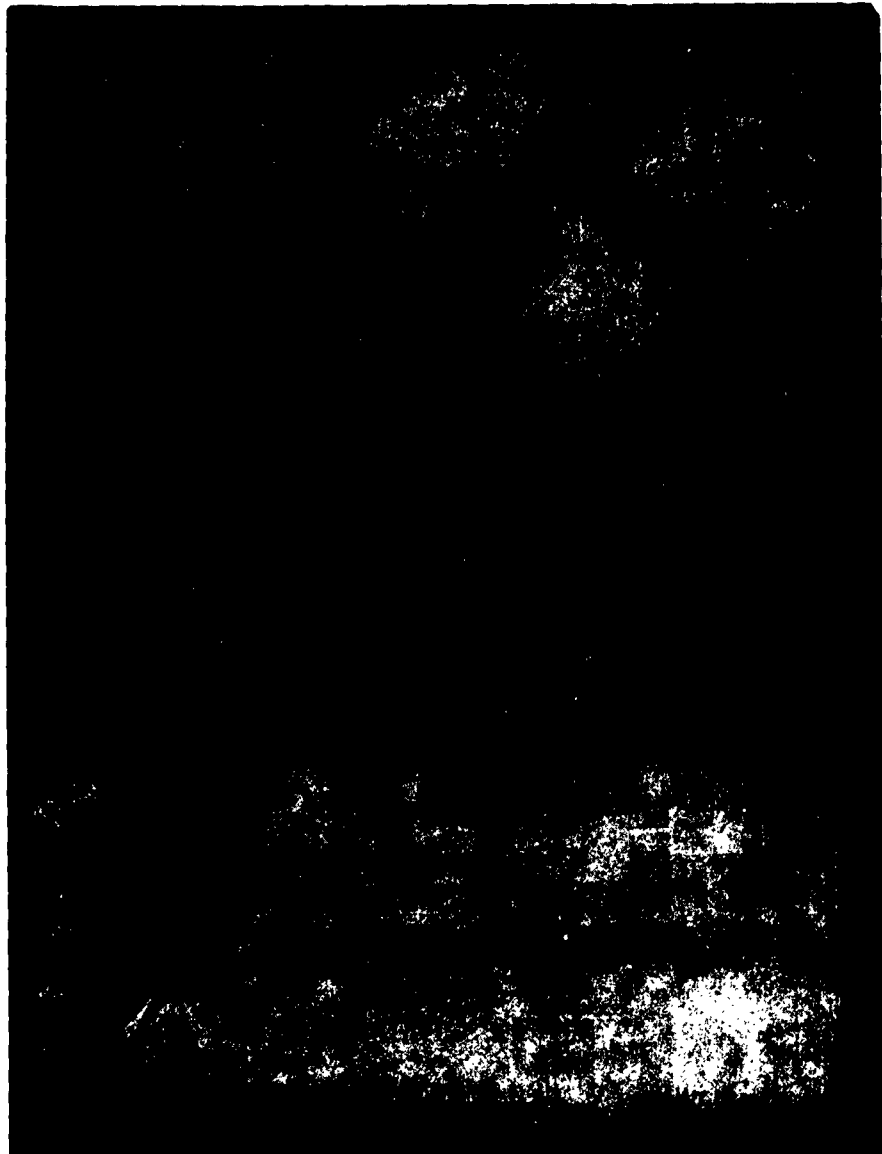


Fig. 2 External Collector Diode

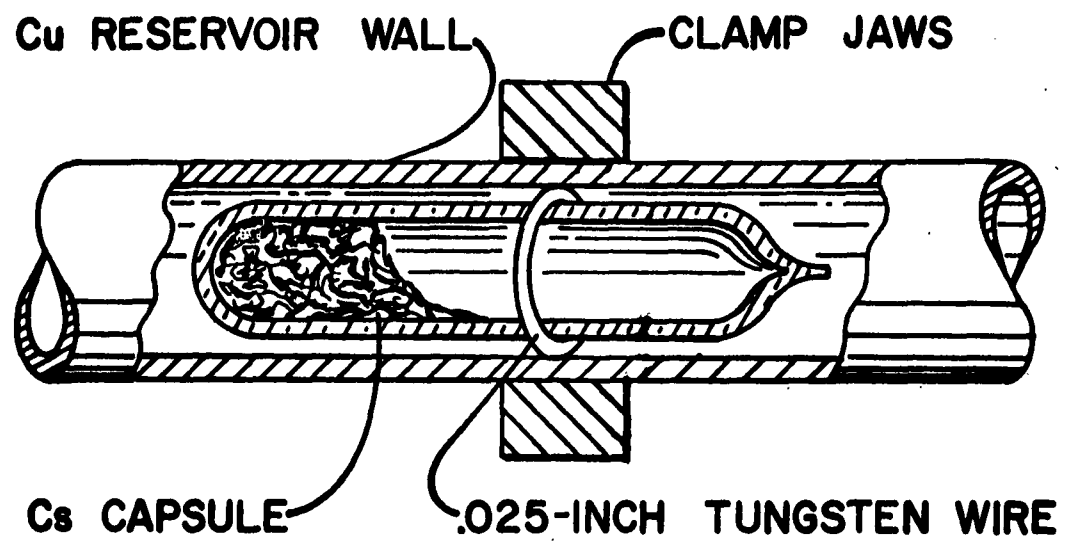


Fig. 3 Method of breaking Cs capsule



Fig. 4 Diode Under Test

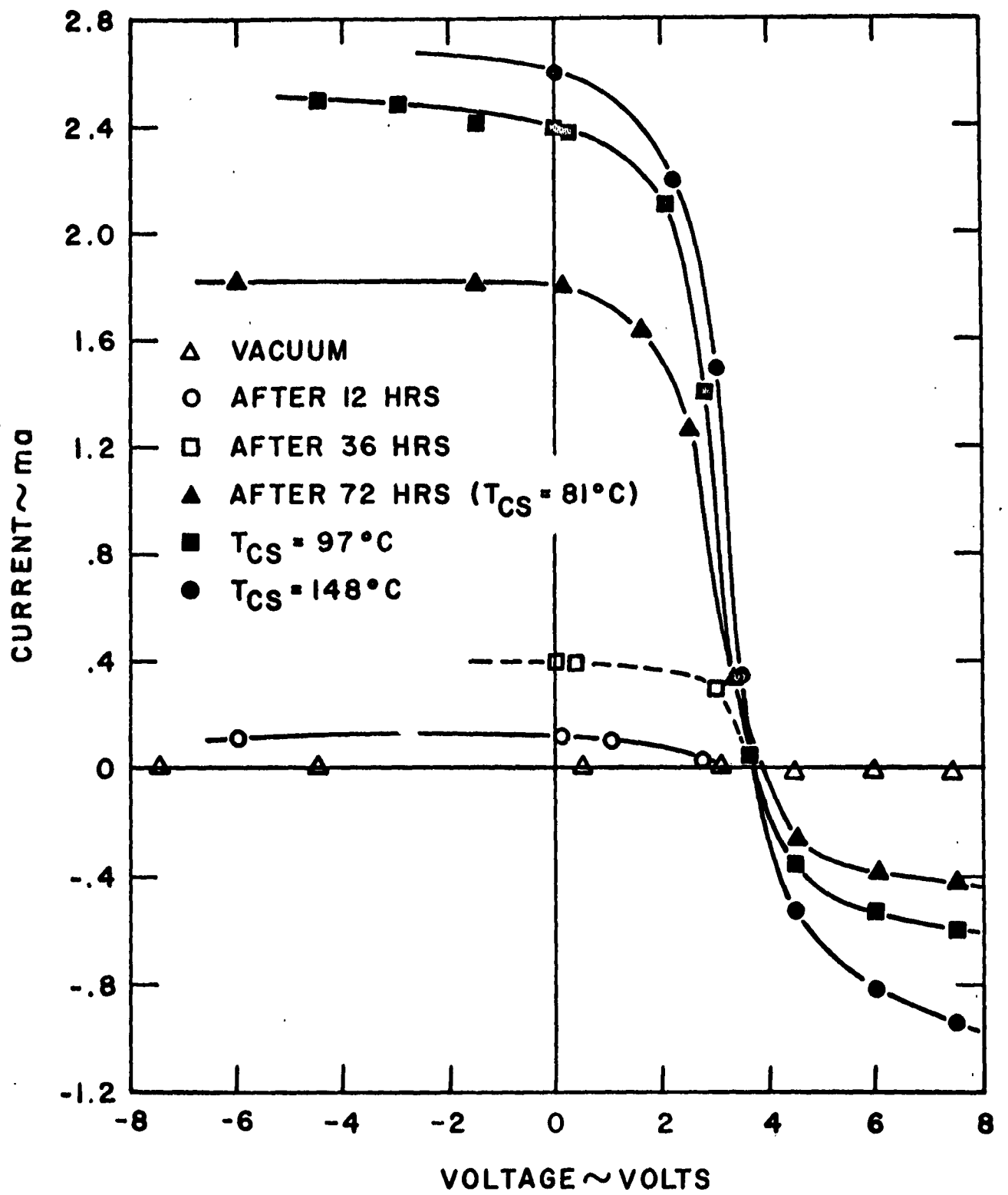


Fig. 5 I-V curves for R3Cs

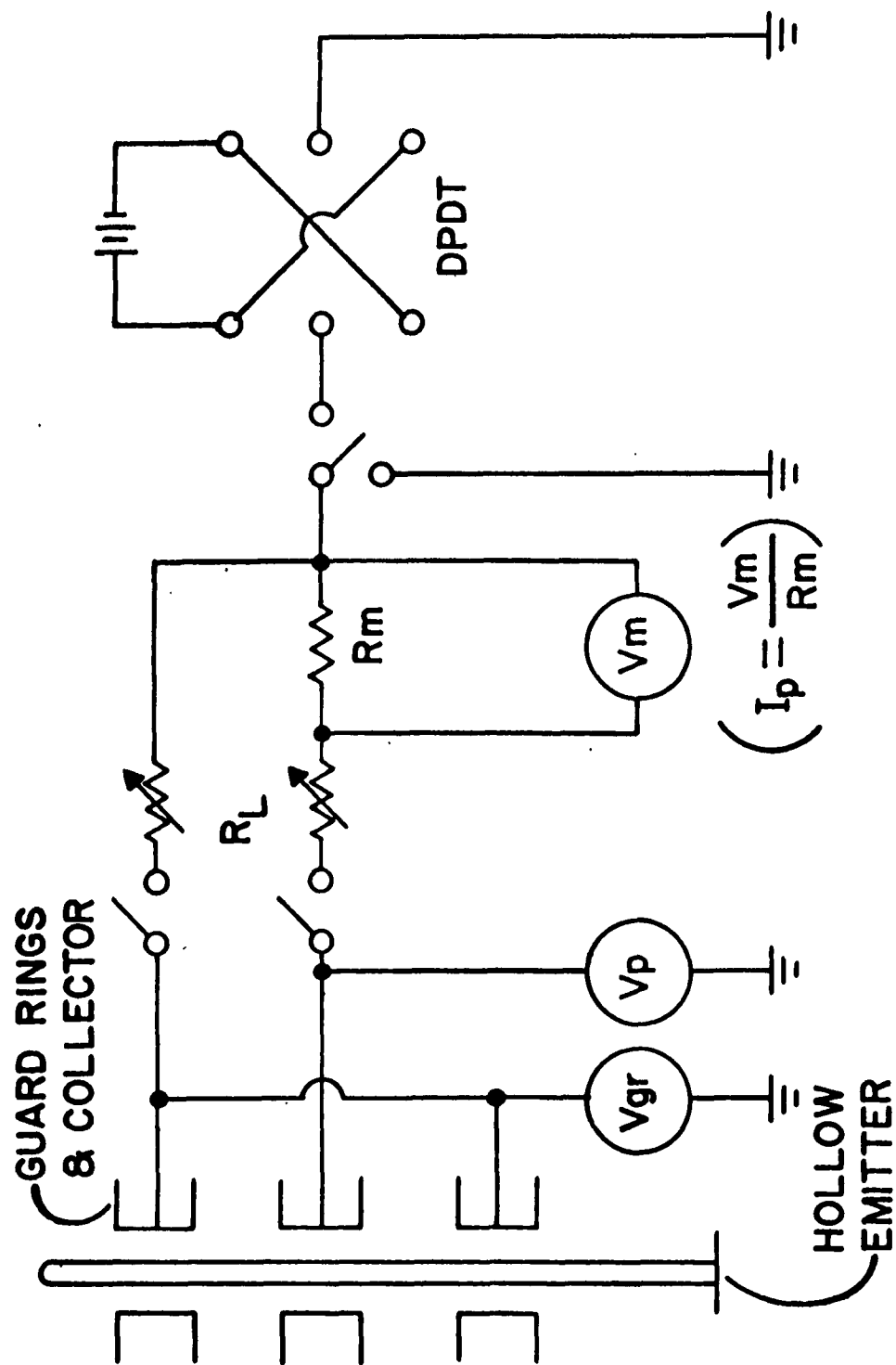


Fig. 6 Schematic of measuring circuit

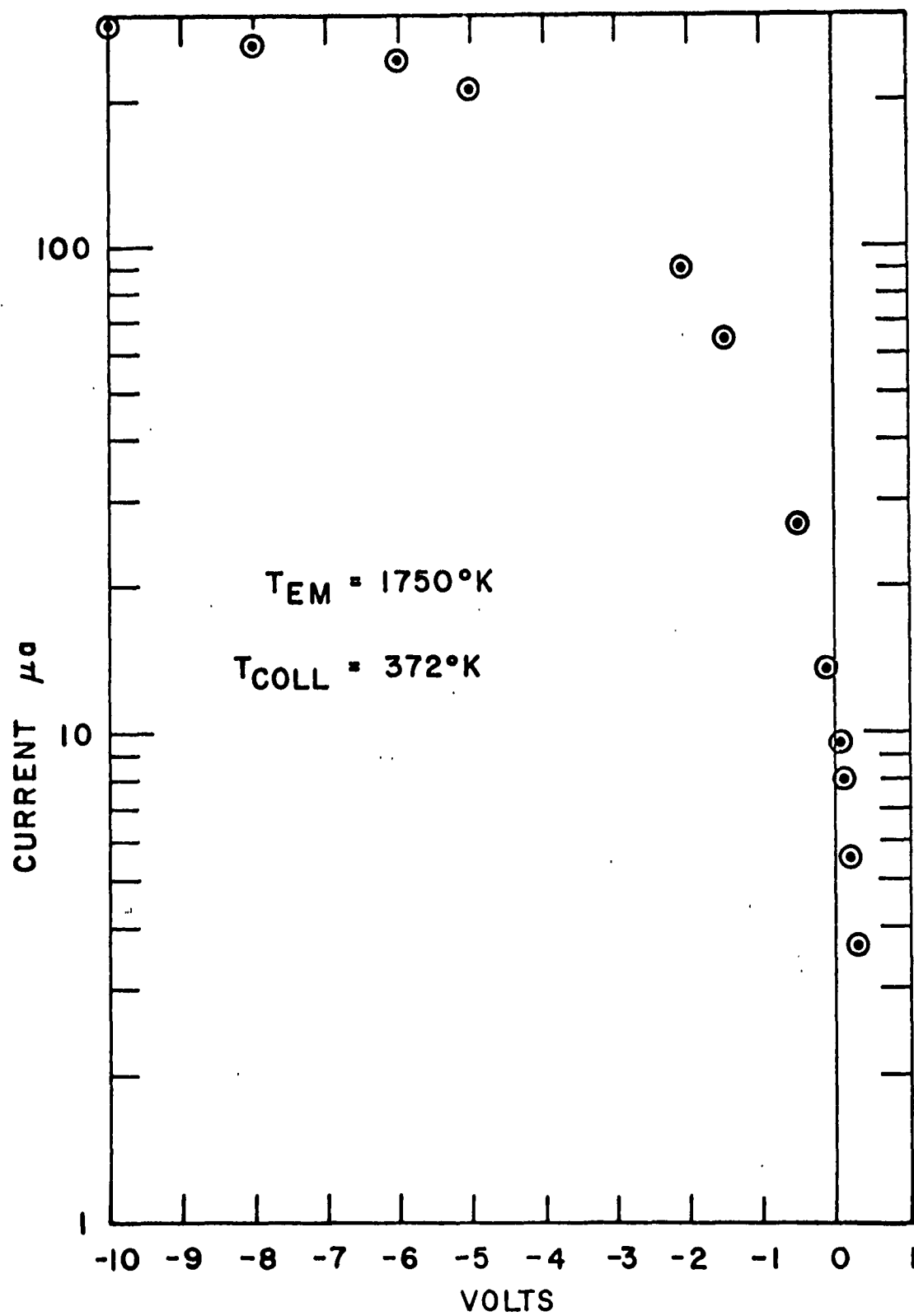


Fig.7 Vacuum I-V curve for diode R5Cs



Fig. 8 Comparison of Emitter Surface Before and Processing



Fig. 9(a) Grain structure before
processing (156 x)



Fig. 9(b) Grain structure after
processing (156 x)

SECTION III

PART B

WEIGHT-LOSS STUDIES

P. F. Woerner
G. F. Wakefield

SECTION III

PART B:

WEIGHT-LOSS STUDIES

P. F. Woerner

G. F. Wakefield

1. Introduction

Space charge neutralization requirements of thermionic diodes necessitate a permeation rate of cesium through tantalum on the order of $0.01 \text{ mg/cm}^2\text{-sec.}$ Measuring this rate by determining the ion current emitted from the tantalum encounters such physical difficulties as ion sheaths. However, since the rate is large enough to be measured through a mass determination, a more direct way is continuous weighing of a heated capsule containing cesium. The weight-loss observed for such a capsule will result from cesium permeation and sublimation of the vessel. With a blank sample (a vessel that did not contain cesium) the sublimation rate was found to be negligible at the temperatures in question. The temperature dependence of the rate was found by measuring rate at a number of temperatures. A semi-log plot of rate vs reciprocal temperature would give an analytic description of the rate, and a linear plot if the measured rate is dependent on a single mechanism. Because the vessels were fabricated from polycrystalline tantalum, both grain boundary and volume diffusion effects would be possible mechanisms leading to permeation.

2. Experimental Work

The permeation vessels were fabricated from 0.001-in. to 0.005-in. tantalum sheet (as shown in Fig. 10), designed so the thin tantalum portion of the sample had a much greater area than the heavier walled stem. A series of spacers kept the evacuated vessel from collapsing when the exterior was exposed to atmospheric pressure. All welding operations were carried out in an inert atmosphere of purified argon resulting in flexible welds even on 0.001-in. material. After the vessels were annealed at 1700°C for 30 minutes in a high vacuum, they were tested on a helium leak detector. A capsule containing 100 mg cesium metal was then inserted in the stem and held up near the permeation cell by slightly constricting the stem. A small cylinder of copper was inserted into the lower tip of the stem; the vessel was stood on this end on a graphite pedestal in a vacuum furnace with the permeation cell and cesium capsule extended into the cold portion of the furnace. After a long period of pumping and outgassing, the copper was melted and allowed to refreeze so as to seal the vessel under a vacuum of 10^{-6} mm Hg. The starting components and the sealed, evacuated vessel were weighed to check the quality of the seal, since the final weight differed from the initial by the weight of the air removed from the vessel. When the stem was straightened, the cesium capsule fell into position just above the copper seal, and the glass was broken to release the cesium into the vessel. The vessel was then suspended in the vacuum thermobalance.

The thermobalance was essentially the one described in a publication in Review of Scientific Instruments,²⁴ with a modified pumping system to obtain better vacua. The modification was a Consolidated Vacuum Corporation MCF300 pump with a liquid nitrogen trap attached directly to the furnace chamber with a short 4-in.-diameter pumping line.

After evacuation, the vessel temperature was slowly raised until a weight-loss was noted. Isothermal weight loss rates were then measured at various temperatures by noting the time required to lose a specific weight (usually 1.5 mg).

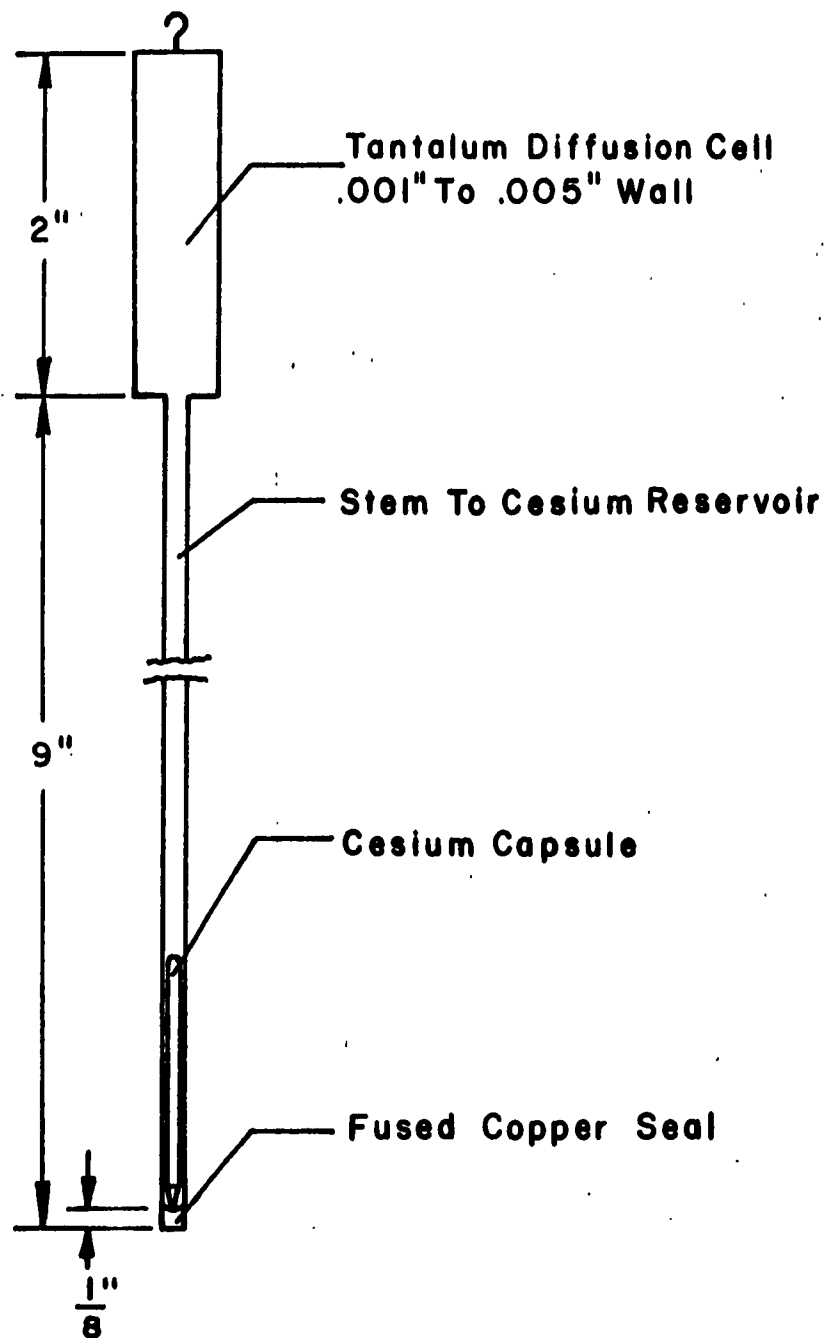


FIG. 10 TEST VESSEL

The cesium pressure in the vessel was the vapor pressure of cesium metal held at the temperature of the stem; thus, the effect of the cesium pressure on the weight-loss rate at a given sample temperature was determined by varying the temperature of the stem.

Following a run consisting of approximately 20 weight-loss points, which corresponds to a weight-loss of approximately 50 mg, the vessel was removed from the furnace and opened with a tubing cutter. The weight of each of the components was determined and compared to the initial values to fix precisely where the weight-loss had occurred. The vessel was helium leak tested again to assure that it was still tight.

All leak testing was done at room temperature; therefore, an experiment was run to determine whether a leak was developed at high temperatures. Conceivably, such a leak could reseal itself upon cooling and thus be undisclosed in the post-run check. A vessel was processed in the usual way, except that it was loaded with a capsule containing helium instead of cesium. The helium leak detector was attached to the foreline of the thermobalance and a normal run was simulated. No weight-loss was observed when the vessel was held at temperature for four hours, and the helium detector did not rise above background value. The vessel was then removed from the thermobalance and placed in a vacuum furnace with the leak detector attached to the foreline. When the copper sealoff plug was melted out, a strong positive test for helium was observed. This showed the presence of residual helium in the vessel and indicated that leaks which were not present at low temperatures did not normally develop at high temperatures.

3. Data

Table II is a summary of the samples tested. Data from each run are shown in the semi-log plots of weight-loss rates vs reciprocal temperature. The numbers at each point are given to denote the sequence in which the run was carried out.

Table II. SUMMARY OF EXPERIMENTAL DETERMINATIONS

<u>Sample No.</u>	<u>Wall Thickness</u>	<u>Process Procedure</u>	<u>Results and Conclusions</u>
CT-1	0.002"	Processed in normal procedure. Attempted to use a gallium bath to control cesium pressure.	Unsuccessful due to changes in height of sample relative to the level of gallium.
CT-2	0.002"	Processed normal procedure	Sample was not completely sealed. Repaired and used as CT-3.
CT-3	0.002"	Processed normal manner. Gallium discarded, replaced by a resistance heater to control cesium pressure.	(See Fig. 11). Noted a continual decreasing weight loss, which was independent of the cesium pressure. No apparent attack of the tantalum. Vessel still helium leak tight after run.
CT-4	0.005"	Processed normal procedure. Run made the same as CT-3. Wall thickness 0.005 in.	(See Fig. 12). Same conclusion as for CT-3. Little effect noted due to increased wall thickness.
CT-4B	0.005"	Rerun of sample CT-4 with new cesium capsule.	Rates began equivalent to final values above. Again continued to decrease. (See Fig. 12).
CT-5	0.002"	Processed normal manner. Vessel annealed in vacuum at 2000°C.	Rates began rather rapid, and evidently the vessel sprang a leak as the rate increased to 0.5 mg/min. Rates independent of cesium pressure.
Blank 1		Vessel processed in normal manner but no cesium capsule.	Weight loss rate at 2200°K which was 102 greater than the vapor pressure of tantalum (see Fig. 13).
Blank 2		A tantalum cylinder was placed between the sample and the heater.	After an outgassing period the weight gain was found to be about 0.2 mg/hr at 2300°C.
CT-5C	0.001"	Processed normal manner.	During startup period the vessel developed a leak.
CT-6	0.005"	Processed normal manner. Annealed at 2100°C-2hrs.	Weight loss rate was extremely low and again decreasing (see Fig. 14), finally coming to an approximate constant weight.

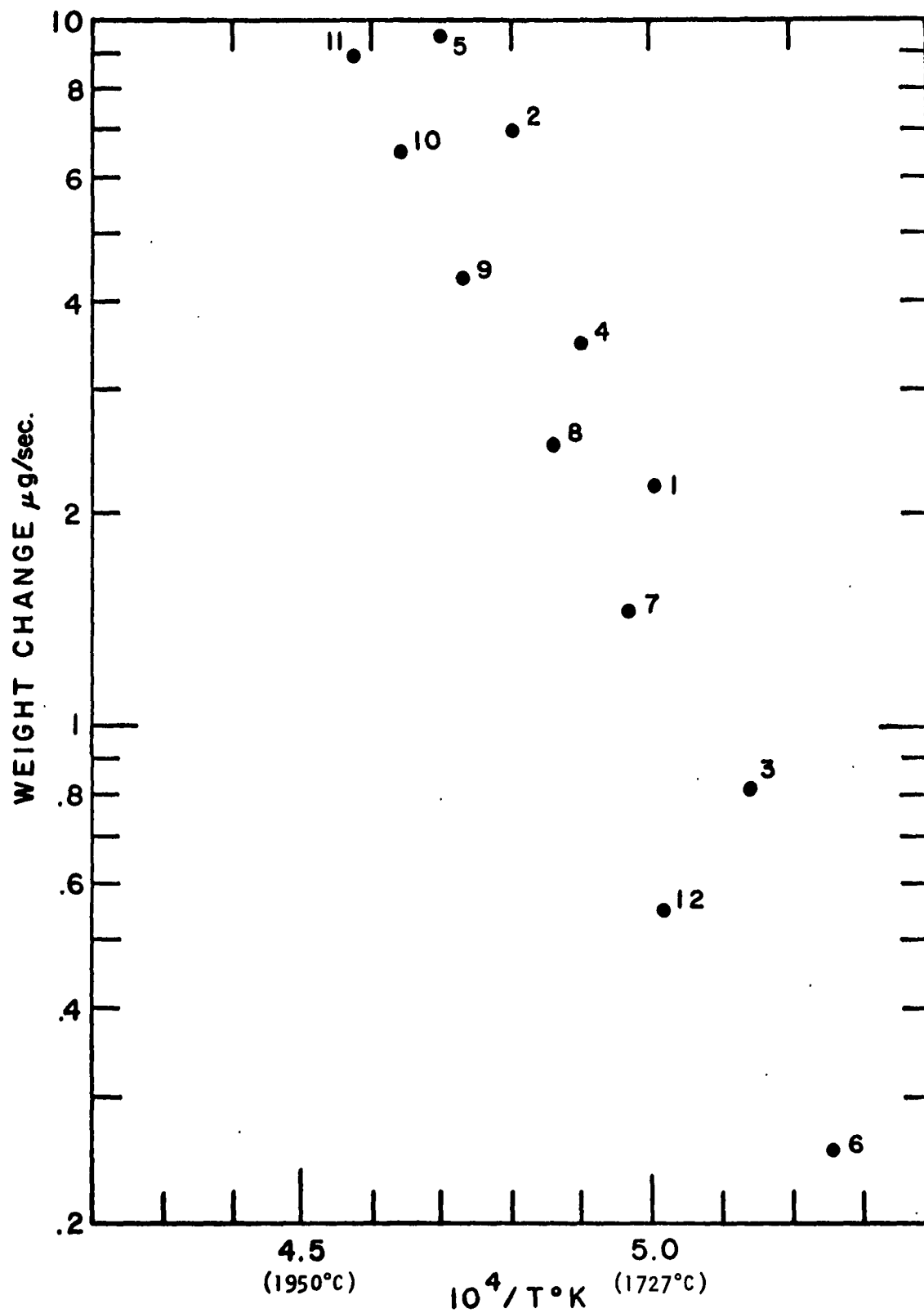


Figure 11 Sample CT 3

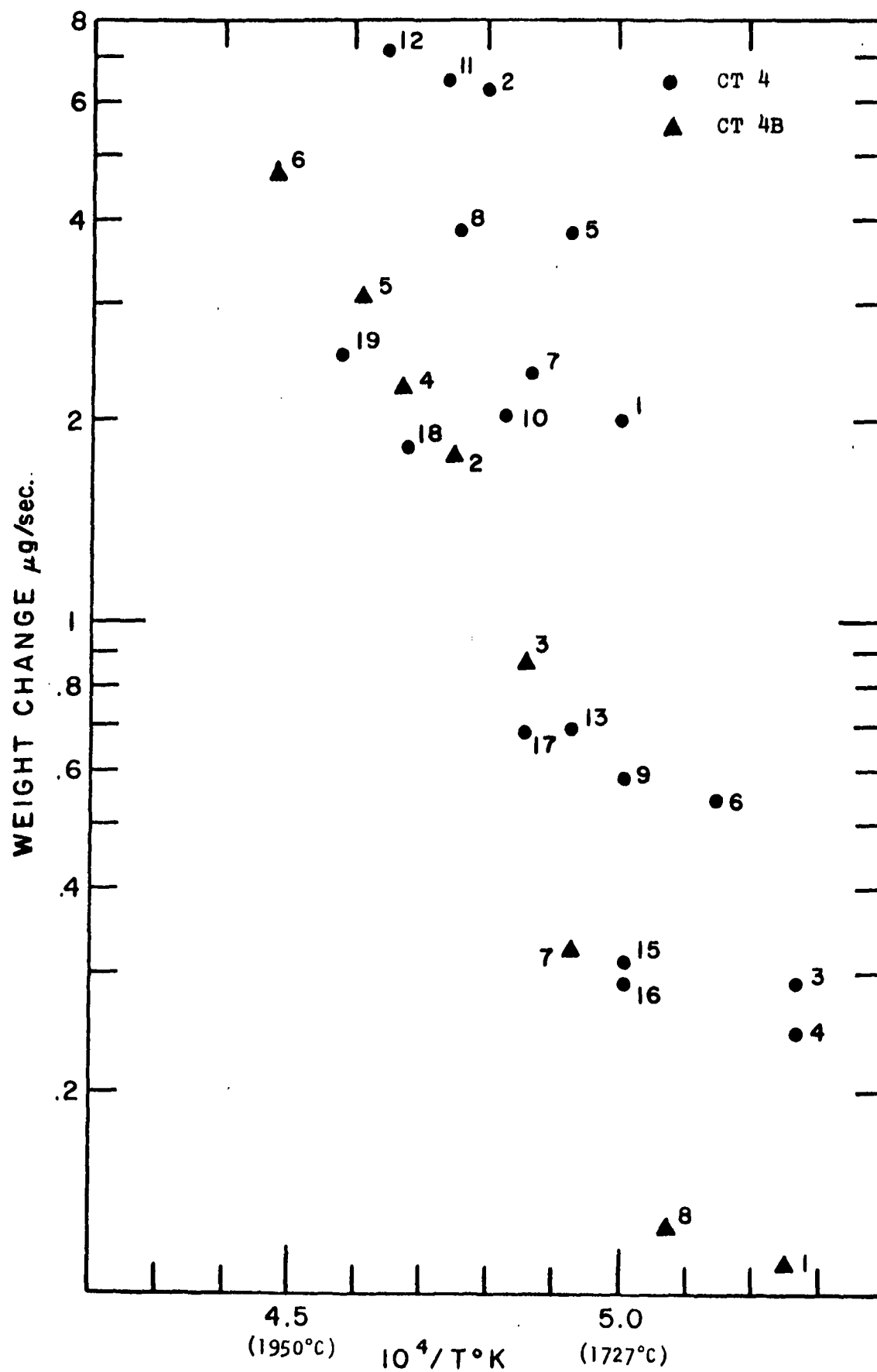


Figure 12 Samples CT 4 and CT 4B

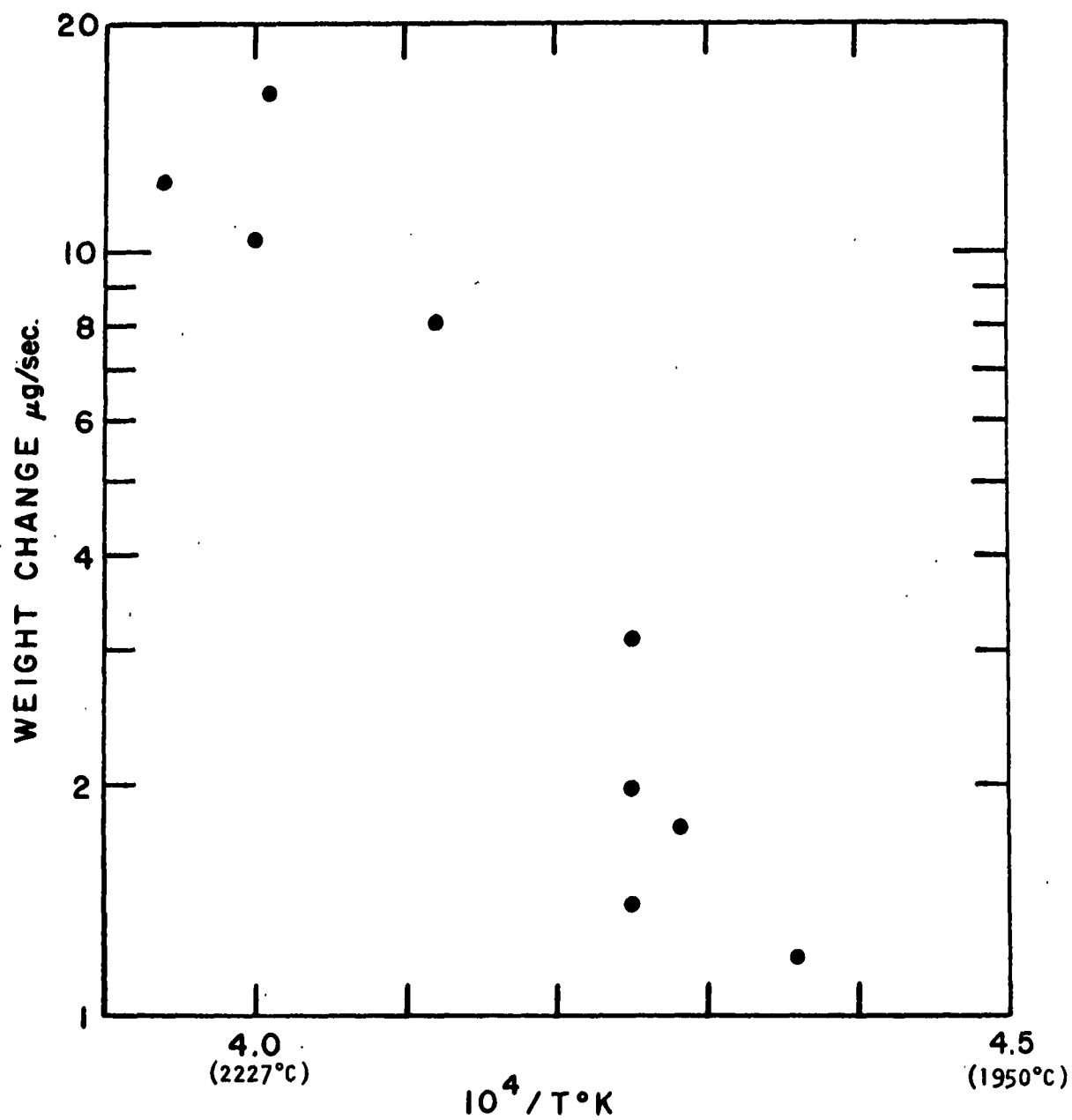


Figure 13 Blank Sample

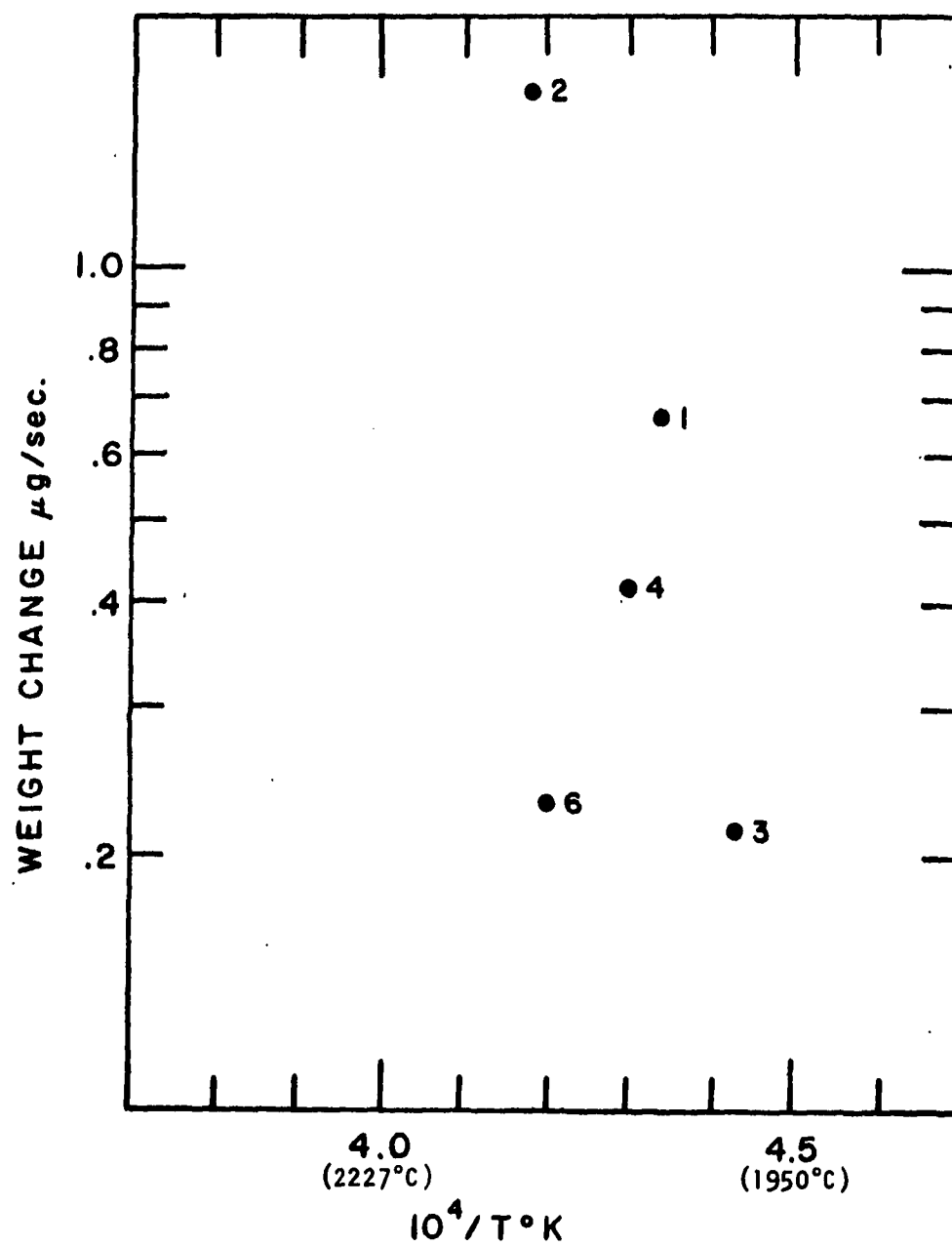


Figure 14 Sample CT 6

4. Discussion

The following conclusions can be drawn from these experiments.

1. The weight-loss observed was caused by cesium permeating through the tantalum. This expected phenomenon was confirmed by the mass checks carried out on the initial and final weights of the vessel components and the tantalum and copper seal plug were found to remain constant within 0.5 mg. Had the weight-loss been from the impurities in the tantalum (while of course they were much less than the total of 50 mg weight-loss per run), it would have been detected at this check.
2. Leaks seemed a problem only rarely, and where one occurred it was detected immediately by a large weight-loss rate.
3. Varying the cesium pressure inside the vessel from 0.2 mm to 13 mm by changing the temperature of the stem while maintaining the vessel temperature constant did not affect the rate. This indicated that even the lowest cesium pressure was sufficient to saturate the tantalum; therefore, the solubility of cesium in tantalum was small.
4. The data show a continual decrease of rate with time for any given temperature. For example, points 1, 9, 15, and 16 for sample CT-4 (Fig. 12) exhibit this continual drop in that the time required to lose 1.1 mg for the sequence were 544, 1707, 3505, and 3530 seconds, respectively.
5. All rates determined with the different vessels were of the same order of magnitude and all decreased in the same way, showing a greater variation within a single run than between runs using vessels of different wall thickness. This was taken to indicate that the tantalum sheet, which was prepared by powder metallurgical techniques, became more impervious to cesium as defects in the structure were annealed out.

These conclusions were substantiated by two experiments. A normal run was completed with vessel CT-4; it was opened, leak-checked and refilled with another cesium capsule. When rerun as sample CT-4A, the weight-loss-rate

continued from where the previous run (CT-4) had finished and again showed a decreasing rate. For the second check, vessel CT-6 was annealed at 2100°C for 2 hours, processed and run in the normal manner. The rate began extremely low and decreased below the sensitivity of this method (less than 0.1 µg/sec).

The permeation rate in grams/sec is given by

$$P = \frac{D C A}{l}, \quad (1)$$

where D = diffusion coefficient - cm^2/sec

C = concentration - grams/cm^3

A = area - cm^2

l = thickness - cm .

From the values of P , Fig. 12, ($\mu\text{g}/\text{sec}$ vs $\frac{1}{T}$) a lower limit for the permeation rate can be represented by a line drawn through the lower points.

From Fig. 12, at 1800°C P would be 0.8 µg/sec. The diffusion coefficient of cesium in polycrystalline material is not known; however, using the diffusion coefficient obtained from the single crystal data $4.9 \times 10^{-10} \text{ cm}^2/\text{sec}$ at 1800°C), a concentration of 0.77 at. % cesium is obtained. This is somewhat larger than expected for the solubility of cesium. Because the diffusion coefficient for polycrystalline material would probably be several orders of magnitude larger, using the true value would make the calculated concentration smaller.

Substituting $D = D_0 e^{-Q/RT}$ into Eq. (1),

$$P = D_0 \frac{CA}{l} e^{-Q/RT}. \quad (2)$$

Assuming a relatively small change in the concentration within a small temperature range, the activation energy for permeation can be calculated from the slope of the $\log P$ vs $1/T$. The activation energy was found to be 4.05 eV (93.4 kcal/mole). This would seem to be too large for a diffusion activation energy in the polycrystalline material.

The weight-loss measured is that of cesium leaving a tantalum surface at approximately 2000°K. The species most probably vaporizing under these conditions would be ions rather than atoms. Taylor and Langmuir²⁵ found the work function for cesium ions from tungsten varied with θ , the fractional coverage of the tungsten, from 1.91 eV for $\theta = 0$, to 3.93 eV for $\theta = 0.67$. The values for tantalum would not be expected to differ greatly from these, and it might thus be postulated that the slope of the permeation curves is related to the ion work function rather than to the diffusion activation energy.

SECTION III

PART C

DIFFUSION OF RADIOACTIVE Cs¹³⁴ IN TANTALUM

P. F. Woerner

G. F. Wakefield

SECTION III
PART C
DIFFUSION OF RADIOACTIVE Cs¹³⁴ IN TANTALUM

P. F. Woerner
G. F. Wakefield

1. Introduction

Although the weight-loss studies outlined in Part B of this section give a direct measure of the permeation rate of Cs through tantalum, which is directly applicable for engineering a converter, they do not give a quantitative measure of the diffusion coefficient. Most thermionic converters employ polycrystalline material as the emitter and, in general, operate above the emitter recrystallization temperature. Thus, in time, the metal will approach singularity. Data reported on the recrystallization of 40% cold-rolled tantalum indicate that at 1670°K, full recrystallization occurs in three to four minutes.²⁶ Consequently, a measure of the diffusion coefficient of cesium in single crystal tantalum represents a lower limit value fairly representative of an emitter after operating at temperature for long periods of time. Cesium diffusion in polycrystalline and single crystal tantalum was measured by standard radioactive diffusion techniques.

2. Experimental

A schematic of the reaction tube used to carry out the diffusion work is shown in Fig. 15. The reaction tubes were fabricated from commercially available tantalum tubing (inner tube 1/4-in. OD, outer tube 5/32-in. ID). A double tube arrangement was employed for protective purposes. Diffusion samples (0.020 in. x 0.1 in. x 0.5 in.) of poly- and single-crystal tantalum were spot-welded to the end cap of the inner tube and annealed at 2000°C in high vacuum for one hour prior to a diffusion run to remove all surface damage, as well as to outgas the material. The single crystal material was lapped and polished before it was vacuum annealed. The samples were carefully spaced in the diffusion tube to prevent welding to the tube walls or to other samples. Crystal singularity was checked by back reflection Laue patterns taken after the vacuum anneal (but prior to a diffusion run) and after a diffusion run to assure that the sample had remained single. The end cap with the samples and a quartz capsule containing 50 mg of radioactive cesium were placed in the tube and the ends welded shut under 1/3 atmosphere of purified argon. The cesium was released by flattening the tantalum tube to crack the quartz capsule; the baffle kept the quartz pieces from contacting the samples. The sample tube was then sealed under 1/3 atmosphere purified argon by welding end caps on the exterior tube.

The diffusion anneal was carried out in a high vacuum tantalum resistance heated furnace. The samples were in the hot zone, where the temperature was measured with a W-W 26% Re thermocouple. A chromel alumel thermocouple measured the temperature of the quartz-containing end of the tube, which was in a cool portion of the furnace. After the furnace was evacuated, the sample temperature was raised to the desired value and maintained there for the specified time. The concentration vs depth relationship of the diffused samples was determined by standard lapping and counting technique. The surface sample area which was lapped was calculated from the density of the sample and a measure of the sample thickness. This is the most accurate method, because the surfaces were parallel. Autoradiographs of the single crystal samples showed the activity was uniformly distributed.

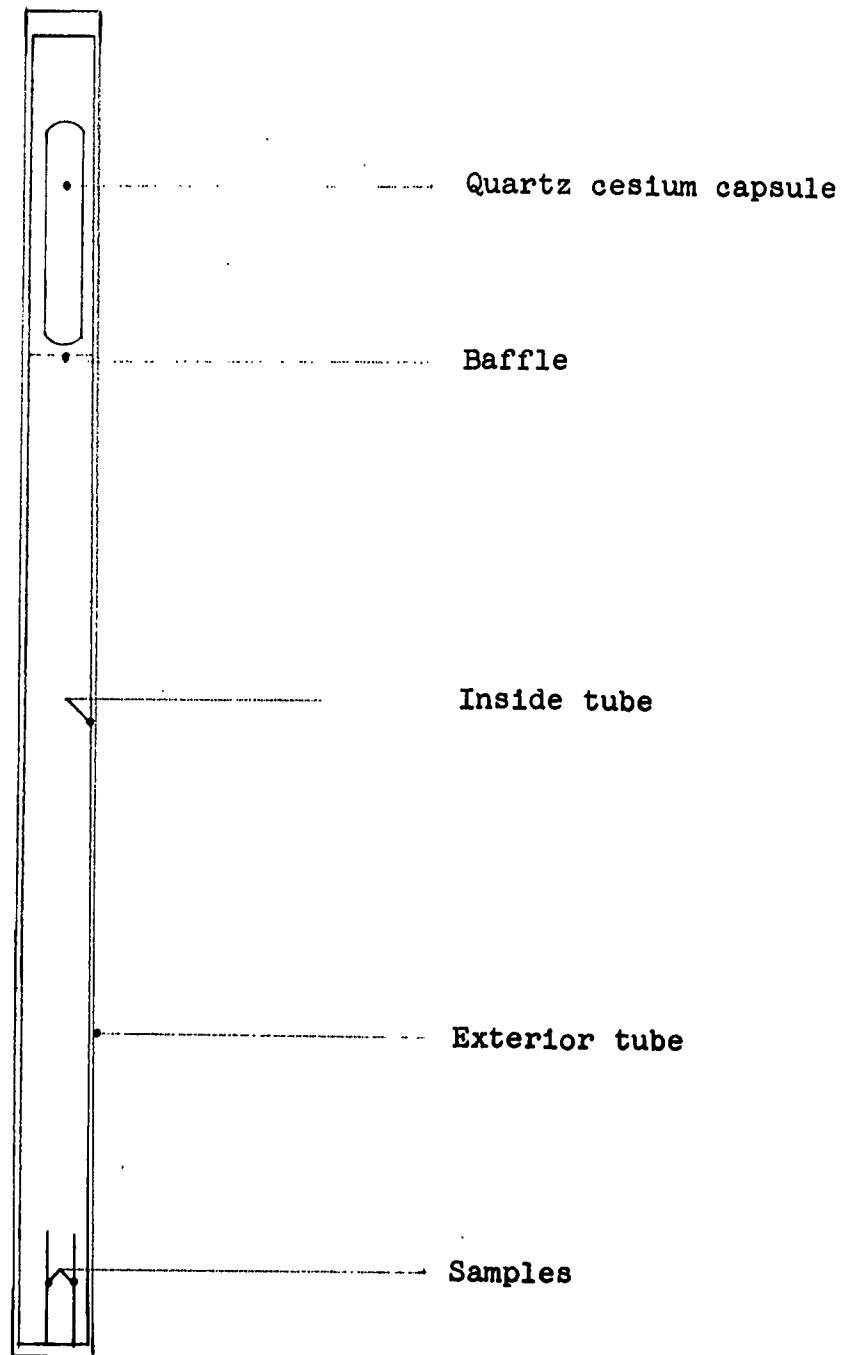


Figure 15 . Cesium Diffusion Tube

3. Experimental Results

a. Single Crystal Data

The manner in which the experiments were run establishing the necessary boundary conditions so that the data treatment and calculation of diffusion coefficient could be carried out by the standard techniques developed for diffusion in a semi-infinite solid. From the second form of Fick's law, if D is assumed to be independent of concentration, the following equation applies:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

Tantalum is cubic and hence, isotropic; consequently, unidirectional diffusion is assumed, and only one diffusion coefficient is required to describe the system. It is assumed that the composition is initially uniform and that the surface is considered to be brought instantaneously to a specific surface concentration of C_s at the beginning of the experiment. It is also assumed that the surface concentration is maintained constant during the experiment. Thus, the following boundary conditions apply:

$$C = C_0 \text{ at } t = 0 \text{ and } 0 < x < \infty$$

$$C = C_s \text{ at } x = 0 \text{ and } 0 < t < \infty$$

The solution to the diffusion equation, Eq. (1), appropriate to the boundary condition is an error function. So long as each lapping depth, Δx , is small compared to $\sqrt{4Dt}$, the diffusant concentration per lap is

$$\Delta C = \frac{C_0}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}, \quad (2)$$

where ΔC is the concentration of radioactive atoms in a lap centered at

x , the distance from the interface, and

D is the diffusion coefficient,

t is the time, and

C_0 is a constant.

From the logarithm of Eq. (2) the following relation is obtained

$$\log \Delta C = - \frac{x^2}{9.2Dt} + \log \frac{C_0}{\sqrt{\pi Dt}} . \quad (3)$$

If the logarithm of the activity, ΔC , is plotted as a function of the square of the distance from the interface, the data should lie on a straight line. The slope of the line described by Eq. (3) is $-\frac{1}{9.2Dt}$, and since t is known, D is readily calculated. The units of D are cm^2/sec . Plots of the logarithm of the activity (counts per minute per cm^3) as a function of the square of the distance in microns for the experimental data are given in Figs. 16 - 23. The diffusion coefficients calculated from the slopes of these curves are given in Table III.

It should be noted that all the curves initially exhibit a high concentration of activity, fall very rapidly, then follow a straight line relationship. The high initial activity is attributed to surface irregularities resulting from thermal grooves formed by thermal etching. It should also be pointed out that the position of the straight lines in Figs. 16 - 23 were determined by placing more emphasis on the initial points after the drop in activity; less emphasis is on the latter points, because they approach background activity.

Variation of the diffusion coefficient with temperature is shown in Fig. 24, in which the logarithm of D is plotted against the reciprocal of the absolute temperature. A straight line relationship is obtained which follows an Arrhenius type equation,

$$D = D_0 e^{-\frac{Q}{RT}} . \quad (4)$$

The activation energy can be calculated from the slope,

$$\text{Slope} = - \frac{Q}{4.575T} . \quad (5)$$

The calculated activation energy for the diffusion process is 1.06 eV (24.5 kcal) and D_0 , the frequency factor for diffusion is $2.47 \times 10^{-7} \text{ cm}^2/\text{sec}$.

Laue x-ray diffraction patterns were taken for each sample before and after the diffusion run to assure singularity of the metal. Typical Laue patterns are shown in Figs. 25 and 26. A typical autoradiograph of a sample is shown in Fig. 27; it was taken to determine whether uniform activity distribution prevailed.

TABLE III

DIFFUSION DATA FOR SINGLE CRYSTAL EXPERIMENTS

<u>Sample Number</u>	<u>Diffusion</u>		<u>Diffusion</u>
	<u>Time (Hours)</u>	<u>Temperature ° C</u>	<u>Coefficient D cm²/sec</u>
27B	24	1400	1.30×10^{-10}
28A	48	1400	1.23×10^{-10}
26B	24	1600	2.65×10^{-10}
27A	48	1600	2.55×10^{-10}
25A	24.8	1800	8.25×10^{-10}
26A	36	1800	3.71×10^{-10}
25B	48	1800	3.23×10^{-10}
120A	24.75	1800	5.42×10^{-10}

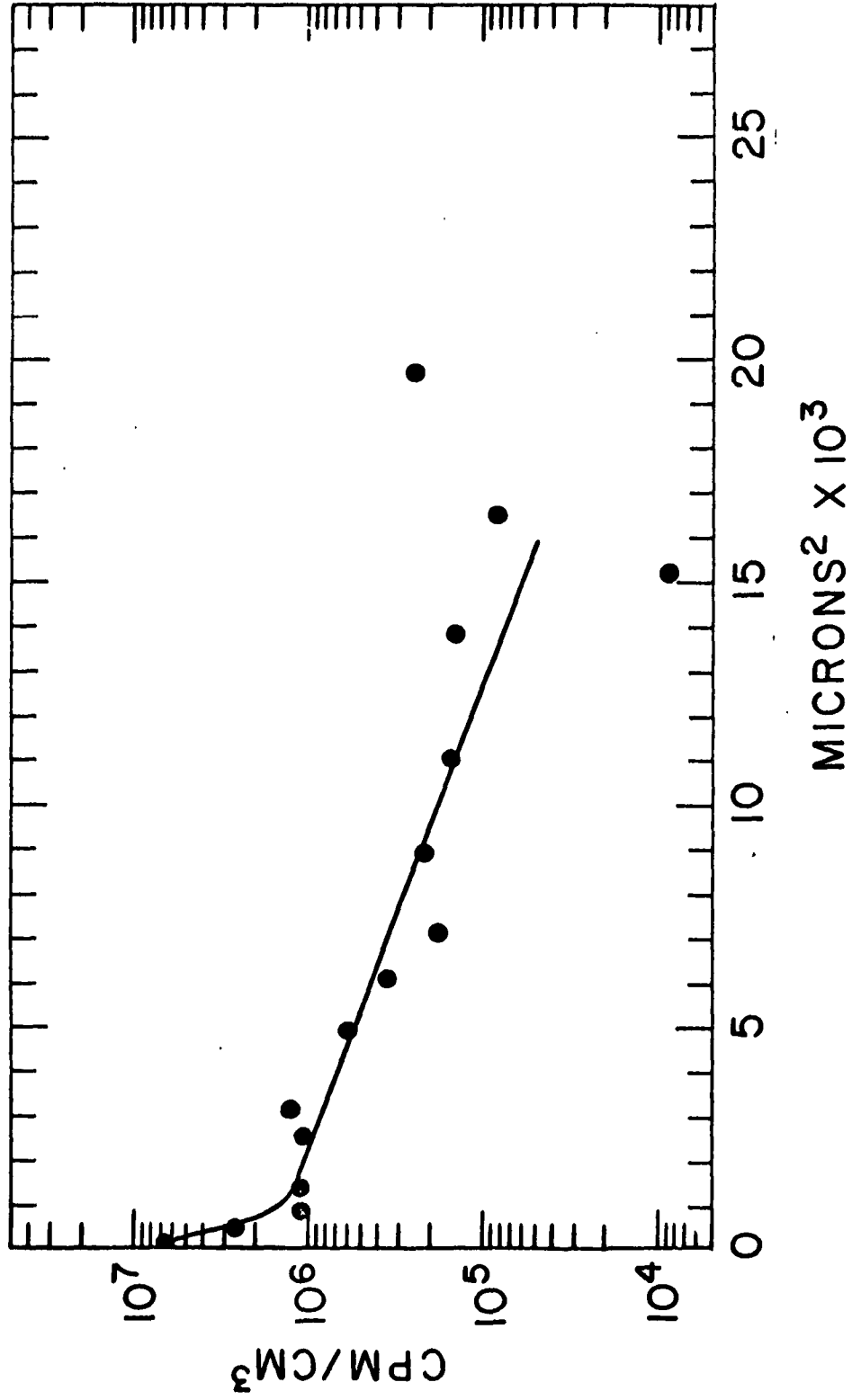


Figure 16 Sample 27B
Diffusion of Cs^{134} in Single Crystal Tantalum. 1400° C, 24 Hours.

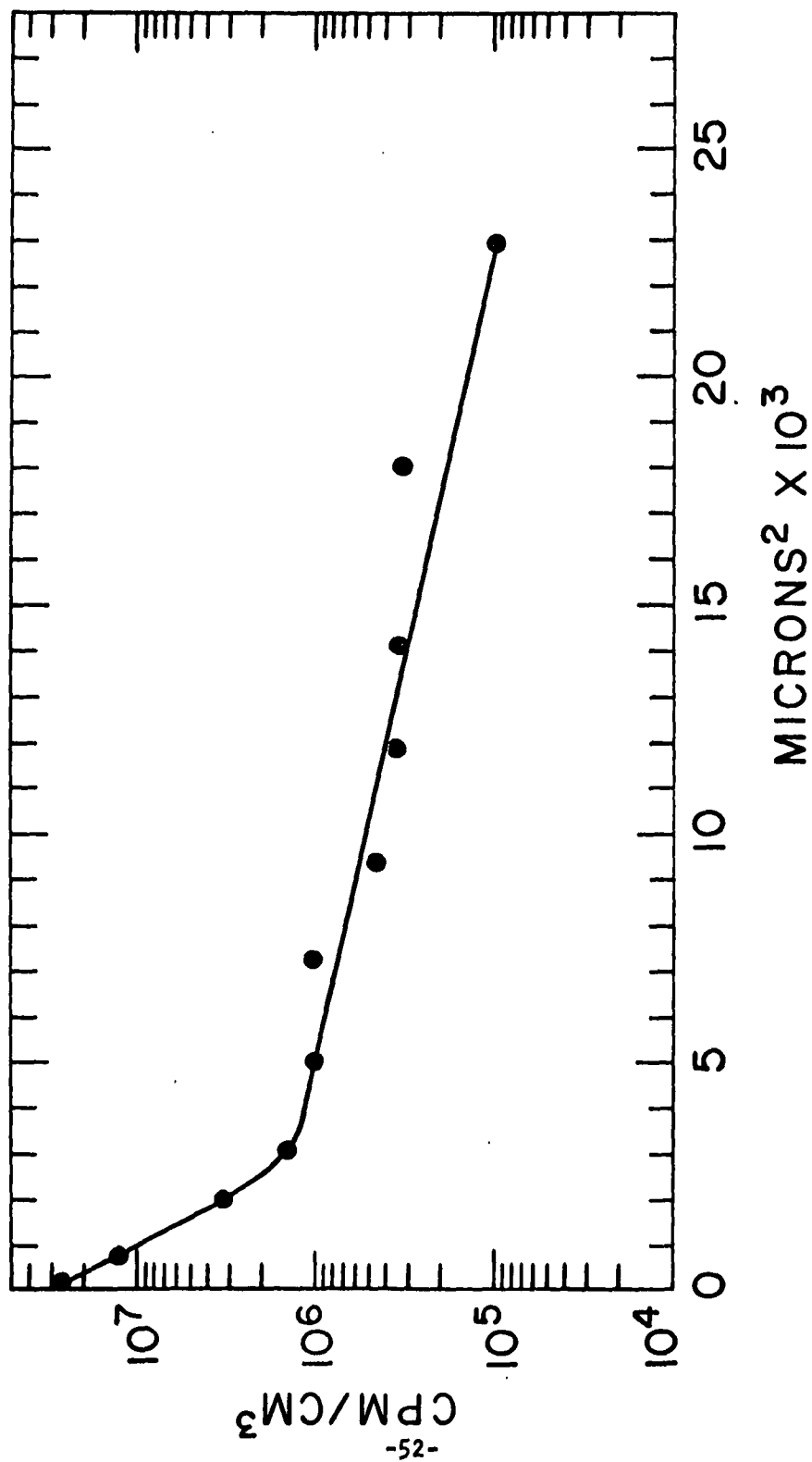


Figure 17 Sample 28A
Diffusion of Cs^{134} in Single Crystal Tantalum. 1400° C, 48 Hours.

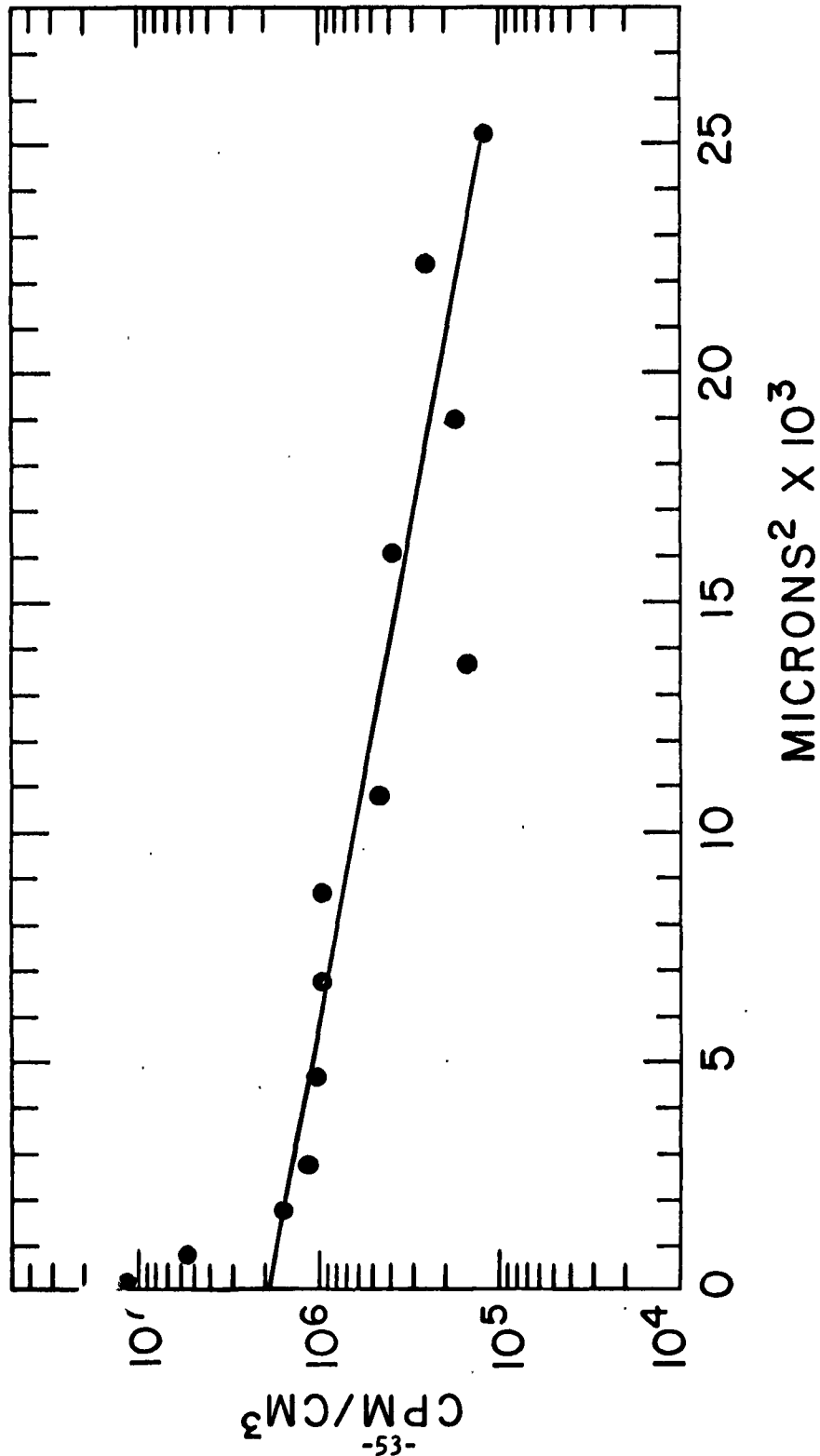


Figure 18 Sample 26B
 Diffusion of Cs^{134} in Single Crystal Tantalum. 1600° C, 24 Hours.

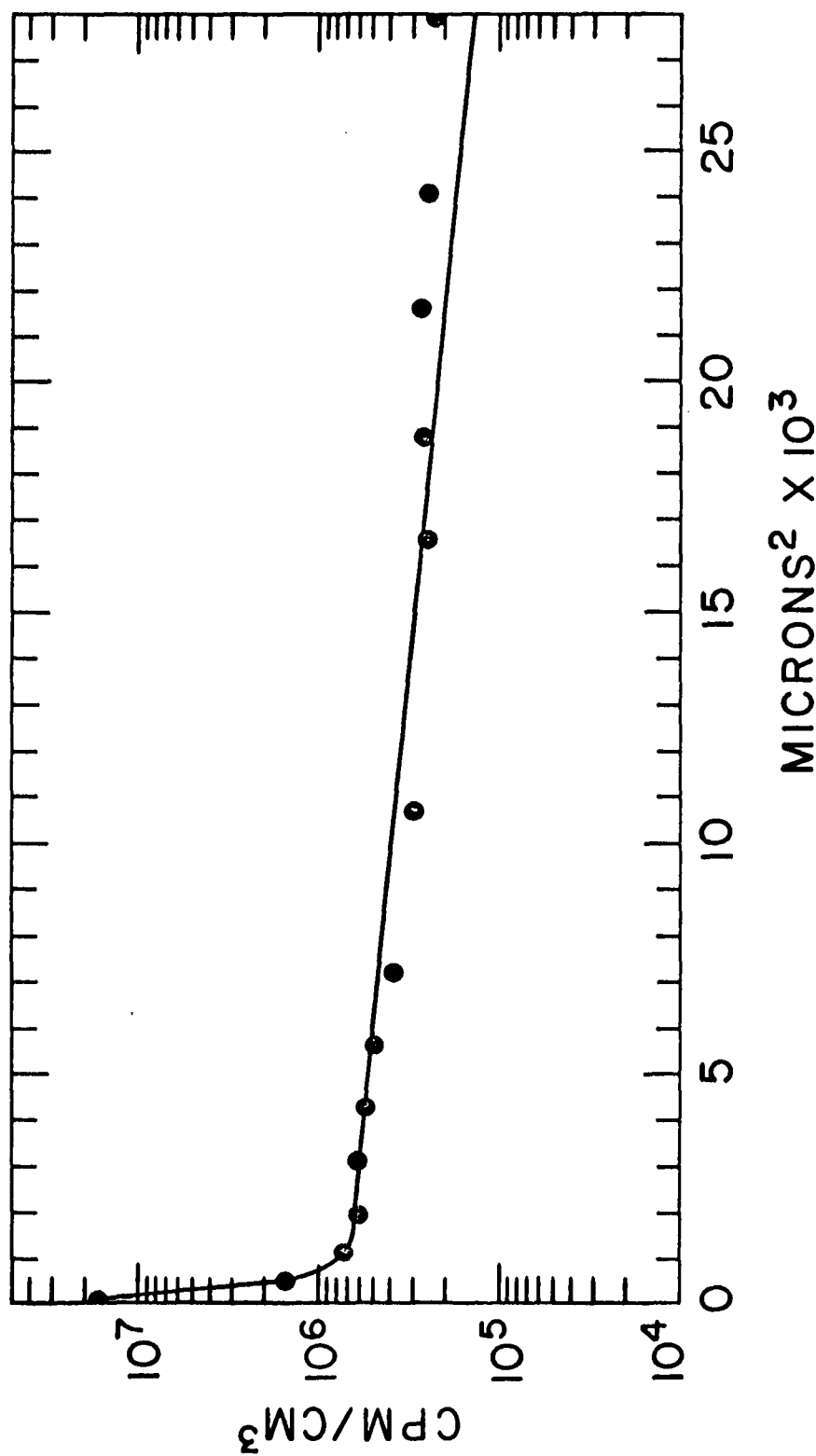


Figure 19 Sample 27A
Diffusion of Cs¹³⁴ in Single Crystal Tantalum. 1600° C, 48 Hours.

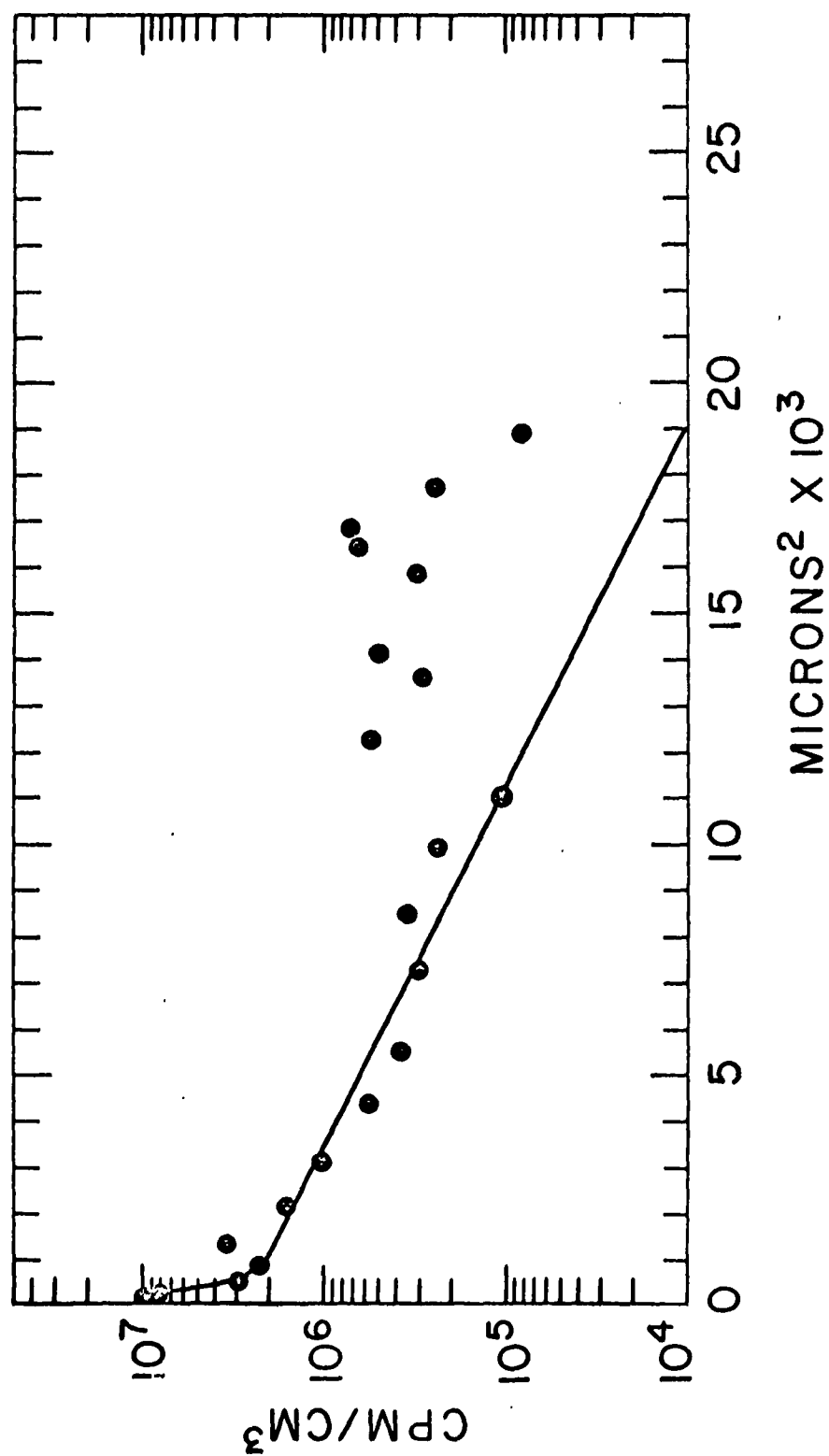


Figure 20 Sample 25A
Diffusion of Cs^{134} in Single Crystal Tantalum. 1800° C, 24.8 Hours.

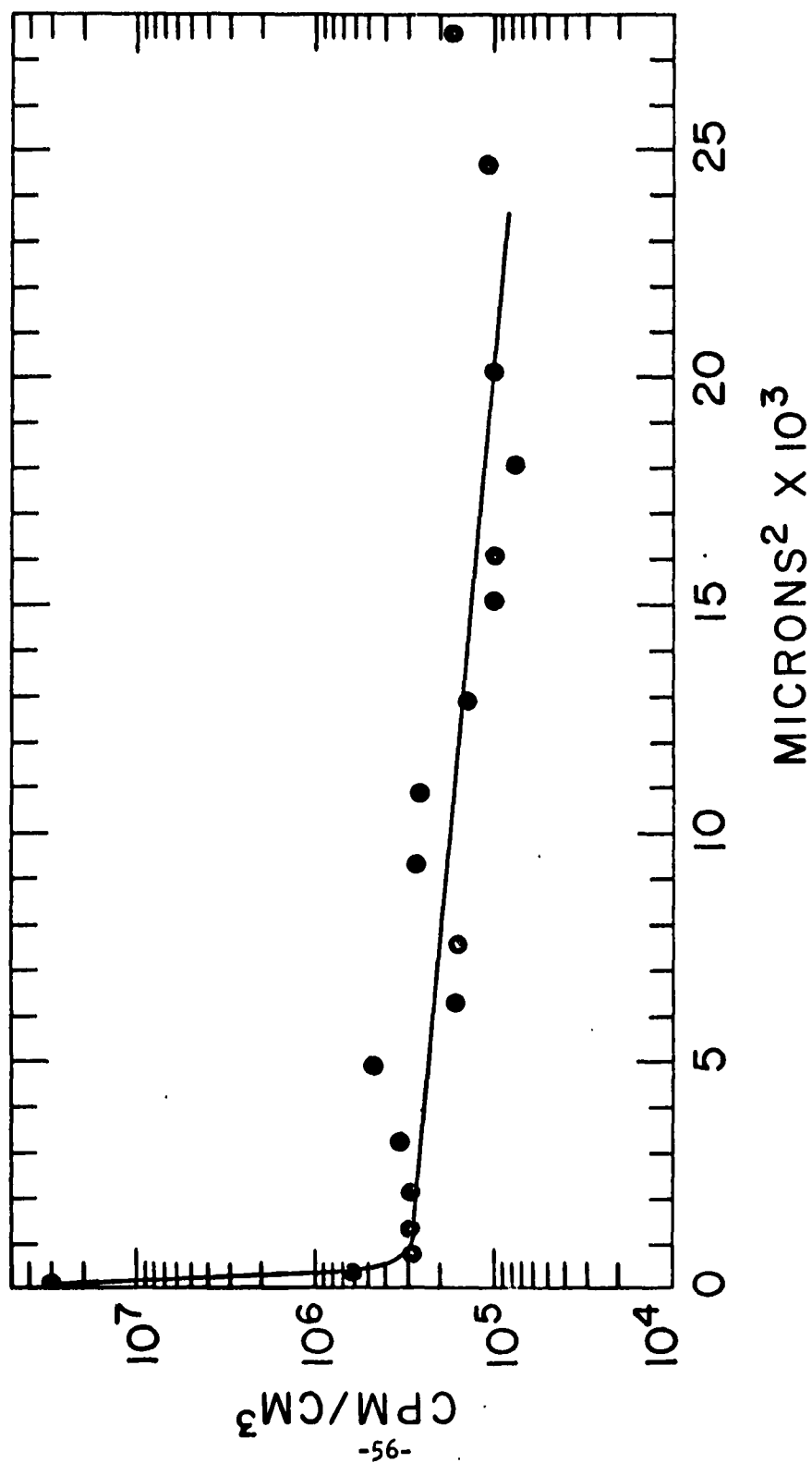


Figure 21 Sample 26A
Diffusion of Cs¹³⁴ in Single Crystal Tantalum. 1800° C, 36 Hours.

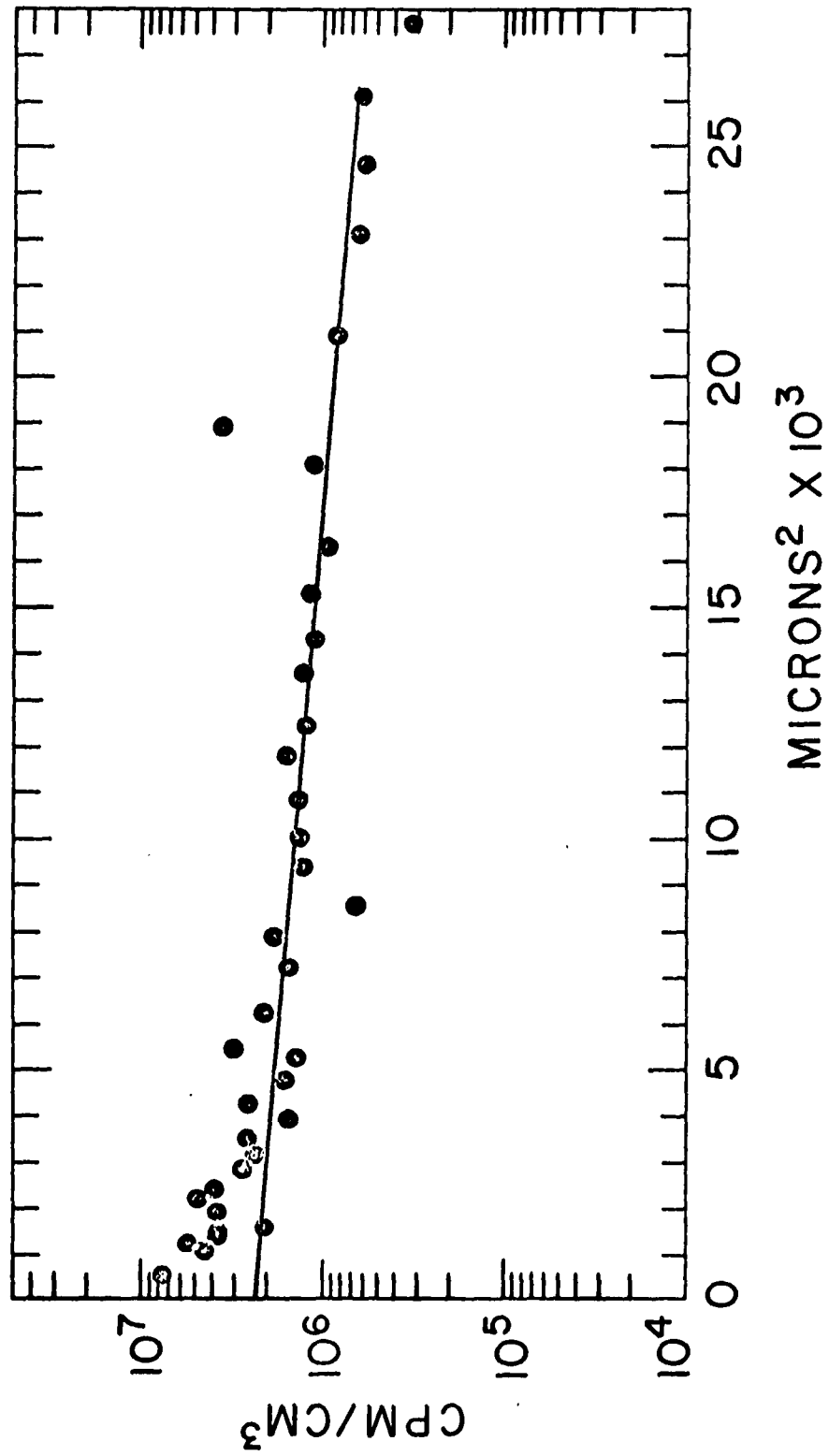


Figure 22 Sample 25B
Diffusion of Cs^{134} in Single Crystal Tantalum. 1800°C , 48 Hours.

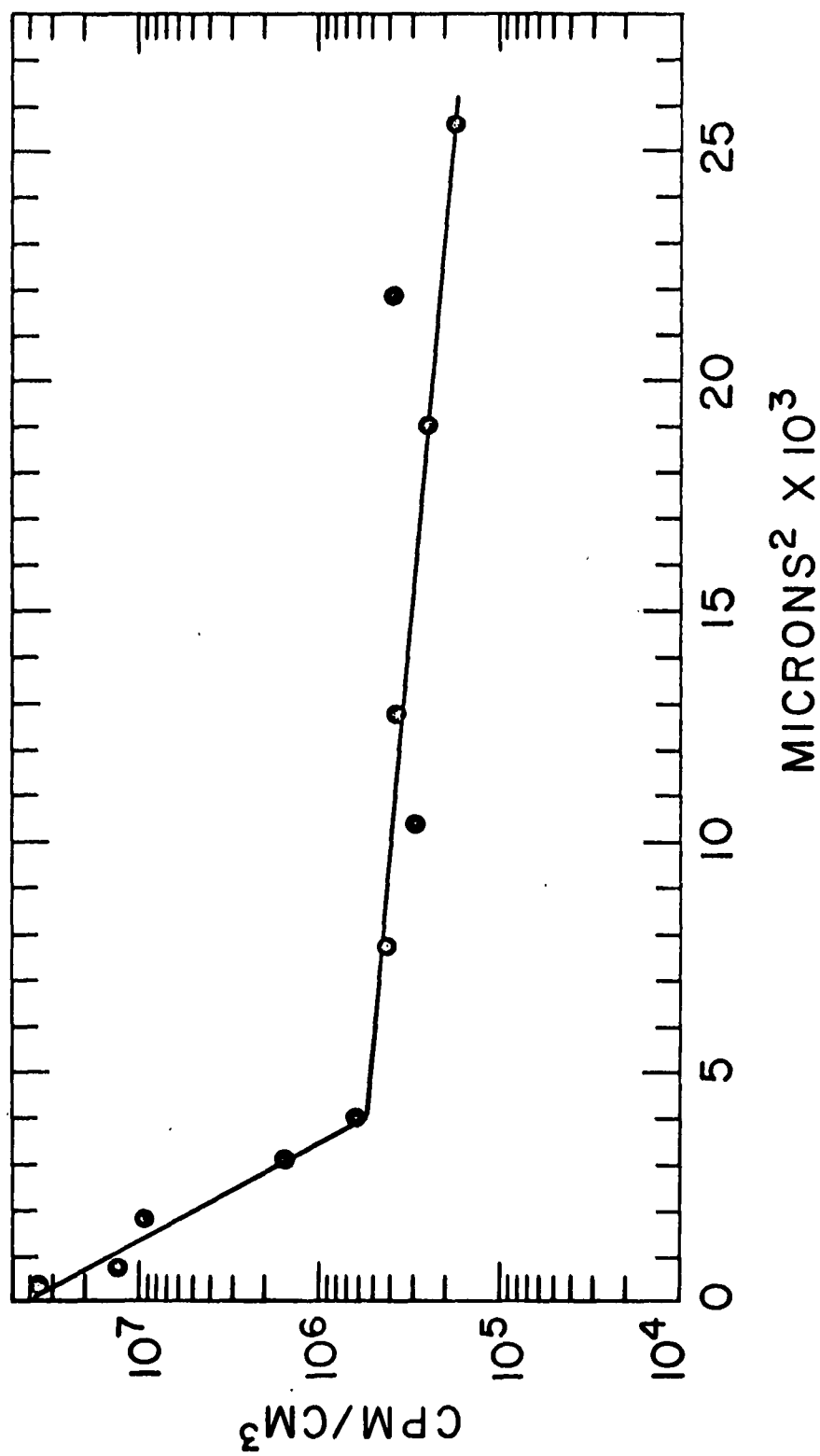


Figure 23 Sample 120A
Diffusion of Cs^{134} in Single Crystal Tantalum. 1800° C, 24.75 Hours.

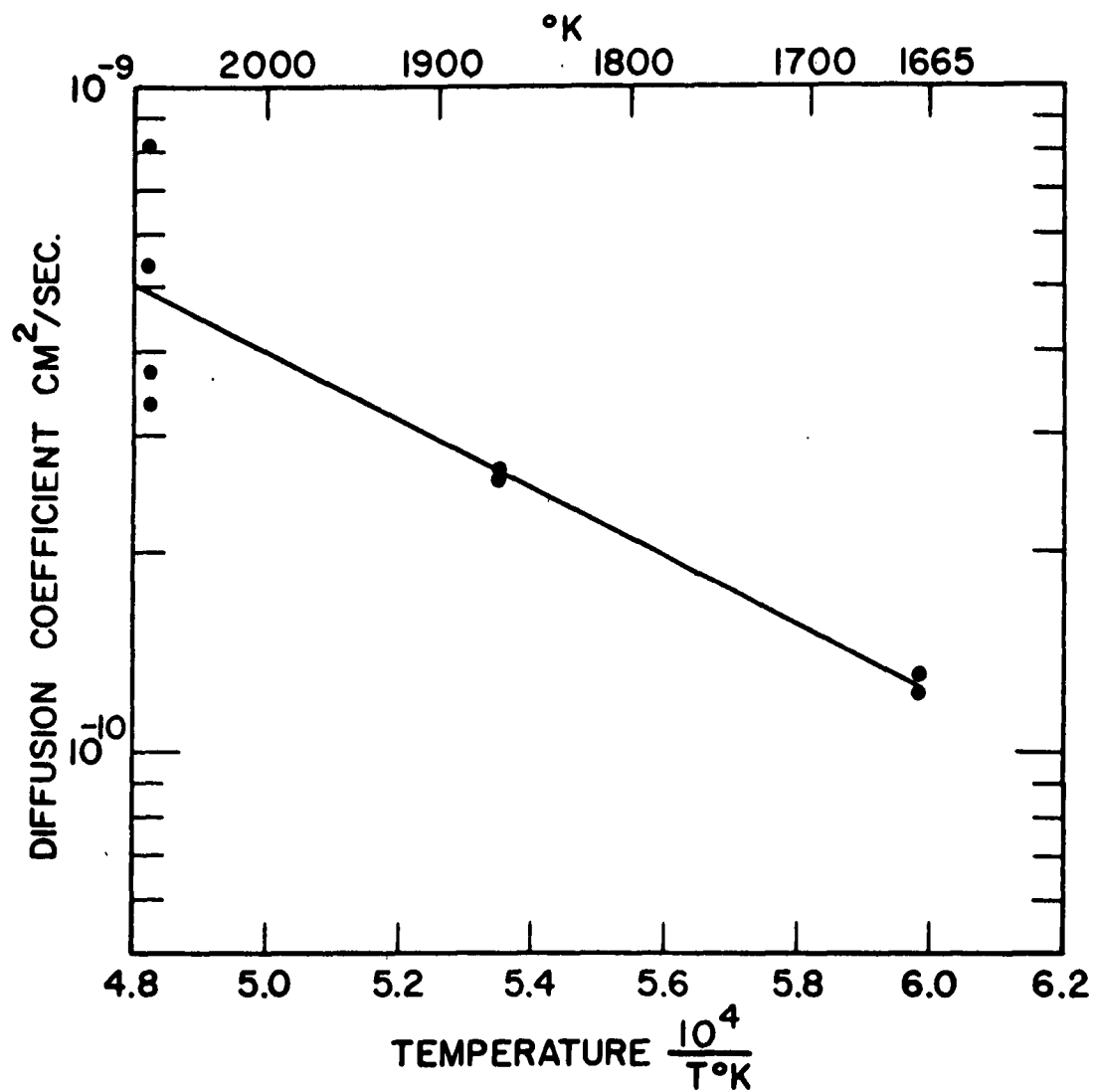


Figure 24 Diffusion Coefficient as a Function of the Reciprocal Temperature

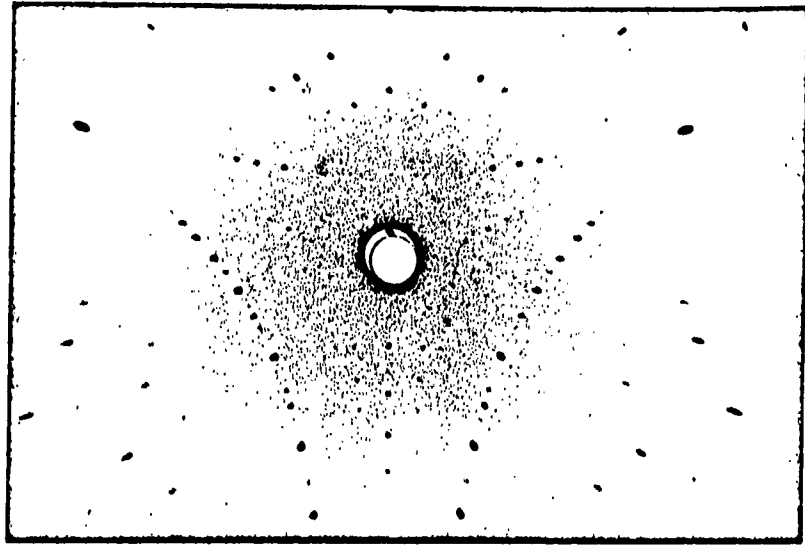


Figure 25 Laue X-Ray Pattern of Tantalum Prior to Diffusion Run

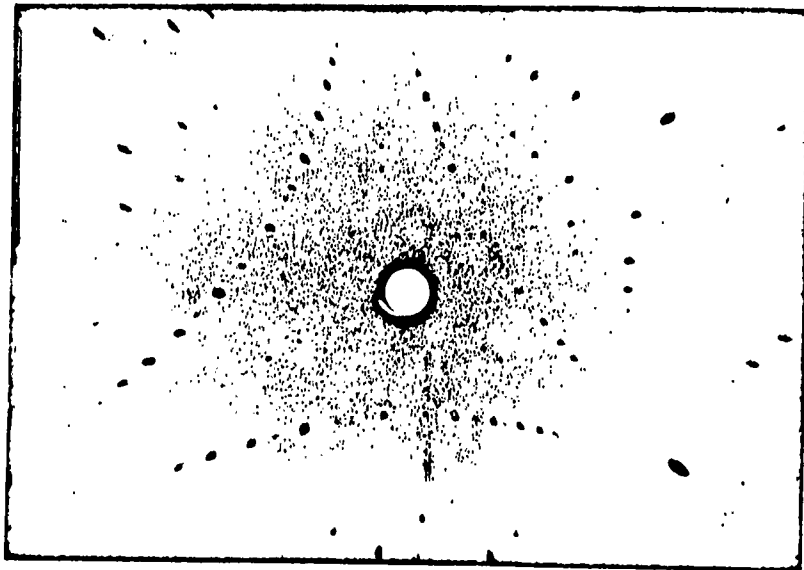


Figure 26 Laue X-Ray Pattern of Tantalum After Diffusion Run

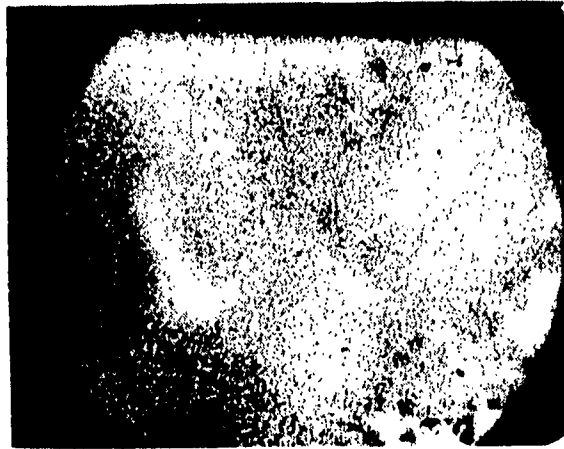


Figure 27 Autoradiograph of Single Crystal Tantalum After Exposure to Cs¹³⁴

b. Polycrystalline Data

Several polycrystalline tantalum samples were run simultaneously with the single crystals to subject them to identical experimental conditions. The data from the polycrystalline samples exhibited considerable scatter; thus, no meaningful calculation of the diffusion coefficients could be made, though several different mathematical applications of diffusion theory were tried. The reasons for this scatter are not immediately explained, but several qualitative reasons can be offered. The material used in this work was as-received and electron beam melted tantalum sheet. Initially, the grain size of this material was fine; however, recrystallization occurred during the diffusion run, as shown in Fig. 28. Here, A is the as-received condition and has a very fine grain size, whereas the grains in B have become considerably larger after diffusion for 12 hours at 1600° C. It is generally accepted that grain boundary diffusion is several orders of magnitude greater than single crystal diffusion in isotropic material. A full description of diffusion in polycrystalline material requires knowledge of D_l , D_{gb} , and D_s , the rates of flow by diffusion in the lattice, grain boundaries and surface, respectively. D_s may vary with the orientation of the surface, and D_{gb} , with both the mutual orientation of the grains adjoining the boundary and the direction of the grain boundary for fixed orientation.¹² If the grain boundaries move as a result of recrystallization or grain growth, any difference between grain boundary and lattice diffusion rates may be so masked that any calculated diffusion coefficient will be of indefinite quantitative significance. Theoretically, the lower limit to the diffusion rate observed in polycrystalline material should be that for single crystal material.

Figures 29 and 30 show data obtained from the polycrystalline material. Both samples were run at temperatures at which substantial grain growth would take place. The diffusion coefficients calculated for these data, applying the same boundary conditions used for the single crystal work, are of the order of 10^{-13} cm²/sec, or about 10^3 lower than the values reported for the single

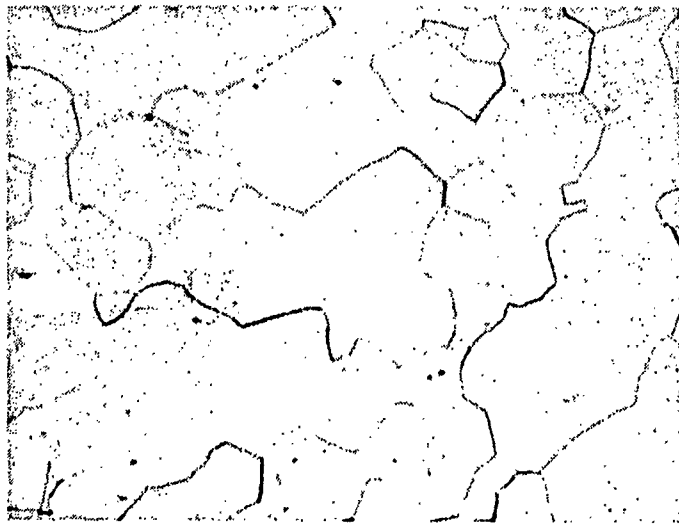


Figure 28 Photomicrographs of As-Received Tantalum Sheet and the Same Material After Diffusion. 294 x, Etched.

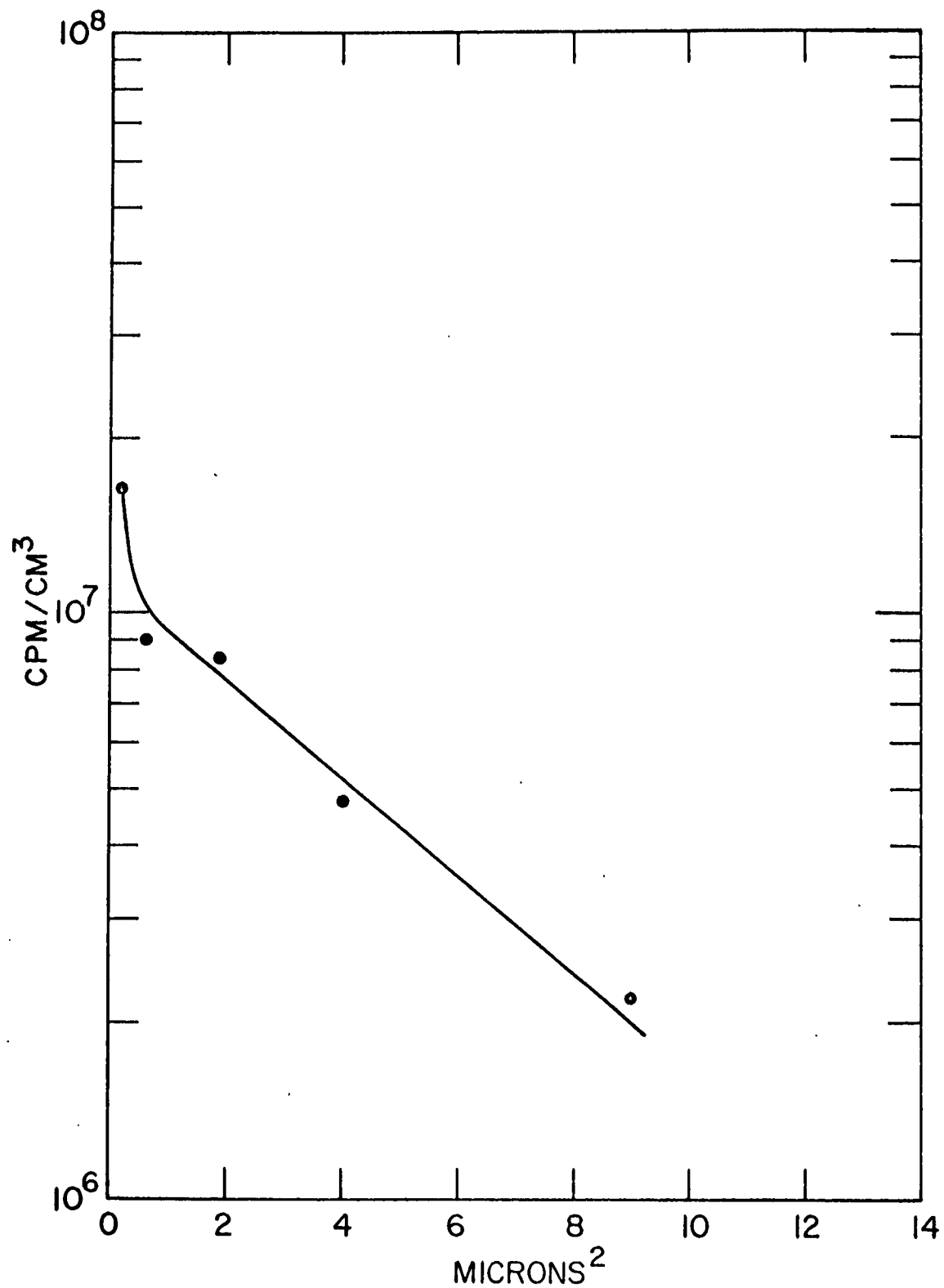


Figure 29 Sample 22A. Diffusion of Cs^{134} in Polycrystalline Tantalum. 1600°C , 12 5/12 Hours.

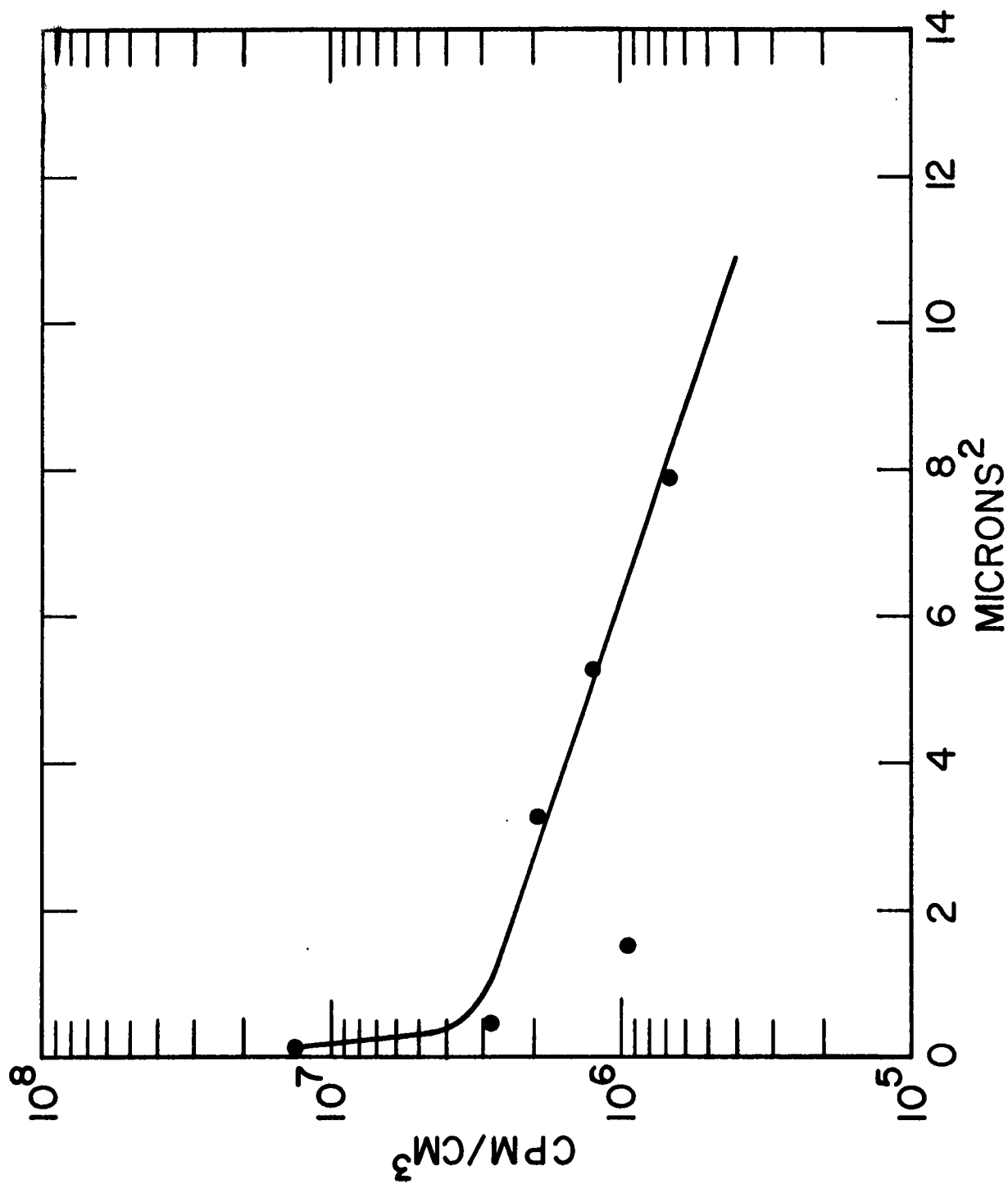


Figure 30 Sample 24A. Diffusion of Cs^{134} in Polycrystalline Tantalum. 1800°C, 11 Hours.

crystals. The activity drops very rapidly to background value within a very short distance, though this was not observed in the single crystal work. A photograph of an autoradiograph of a polycrystal sample, Fig. 31, shows non-uniform distribution of the activity. There is evidence (note left side of the sample) that the activity concentrated at the grain boundaries. This is to be expected; however, it is not known how the activity is dispersed if the grain boundary is annihilated.

Fisher's analysis, as described in Section II of this report, may also be applied to the polycrystalline data at 1800° C in cesium vapor for 1.59×10^4 sec. This analysis gives

$$\frac{D_l}{D_{gb}} = 4.5 \times 10^4 \text{ cm}^{-1}$$

Assuming a grain boundary thickness of 5 \AA , this yields a diffusion coefficient of $2.1 \times 10^{-7} \text{ cm}^2/\text{sec}$ in the grain boundary itself (D_{gb}).

Many mechanisms have been described to explain diffusion in metals. From a consideration of the size of the diffusing atoms or ions and the lattice into which they are diffusing one can rule out a number of reported mechanisms. For interstitial diffusion the cesium must fit into either the tetrahedral or octahedral interstice for tantalum. The tetrahedral and octahedral voids for tantalum have radii of 0.417 \AA and 0.220 \AA , respectively. Cesium atoms or ions, radii 2.63 \AA and 1.69 \AA , respectively, cannot be placed in these voids even with extreme lattice distortion. Consequently, interstitial diffusion is unlikely. Possible mechanisms which could be operative are of the vacancy types commonly observed in self-diffusion or an exchange ring mechanism described by Zener.¹³ The low activation energy observed for cesium diffusion in single crystal tantalum is not typical of self-diffusion, because this is generally very slow, with large activation energies for body-centered cubic metals.

Because neither the vacancy concentration nor the rate at which vacancies are generated is known, one cannot determine the sole diffusion mechanism.

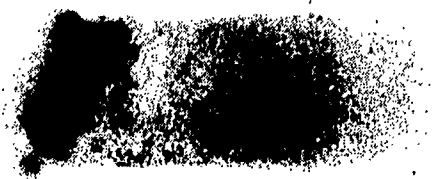


Figure 31 Photograph of an Autoradiograph of Polycrystalline Tantalum After Exposure to Cs^{134} . Note Accumulation of Activity at the Left End. Magnification 27 x.

SECTION IV

COMPATIBILITY OF RESULTS AND CONCLUSIONS

SECTION IV

COMPATIBILITY OF RESULTS AND CONCLUSIONS

The basic question to be answered is: Can the permeation of cesium through tantalum be large enough to provide space-charge neutralization for an electron current as large as 5 amps/cm^2 ? This requires 10 ma/cm^2 , or $13.3 \mu\text{g/cm}^2\text{-sec}$, of cesium ions. With respect to this question, ion-current measurements gave inconclusive results; results of the weight loss and tracer studies are not fully compatible, but both cases firmly answer "no" to the question.

A. Radioactive Tracer Experiments

Tracer data on single tantalum crystals give an average diffusion coefficient of $4.9 \times 10^{-10} \text{ cm}^2/\text{sec}$ near 1800°C . The temperature dependence of this data yields an activation energy for diffusion of 1.06 eV and a D_0 of $2.47 \times 10^{-7} \text{ cm}^2/\text{sec}$. Using a tantalum wall thickness of $2.54 \times 10^{-2} \text{ cm}$ for a hollow emitter and a maximum cesium concentration in tantalum of 0.1 at. \% , the permeation ion current would be $0.17 \mu\text{a/cm}^2\text{-sec}$, a result far too low for neutralization of useful electron currents. Certainly there are no errors in the experiment or in the conversion to permeation rate which could increase the ion-current by the 6×10^4 factor necessary to get an ion current of 10 ma/cm^2 . This definitely rules out practical use of this diffusion phenomenon in single crystal tantalum.

The magnitude of the cesium diffusion coefficient in single crystal tantalum should not be unexpected. It is several orders of magnitude larger than self-diffusion in tantalum and is similar to thorium diffusion in tungsten.^{14,27} If anything, it is larger than expected.

The diffusion data in polycrystalline tantalum were erratic, probably because of variations in grain diameter and grain growth during diffusion. The erratic nature of the data was demonstrated by autoradiographs of the tantalum surfaces after diffusion. Fitting these data to a Gaussian distribution (as was done for single crystals) gives diffusion coefficients a

a factor of 10^3 less than in single crystals. This result is theoretically unacceptable. Applying the analysis of Fisher yields a diffusion coefficient of $2.1 \times 10^{-7} \text{ cm}^2/\text{sec}$ at 1800° C in the grain boundary. This could be a more correct interpretation of the polycrystalline data. Little weight was given to the polycrystalline results because of their erratic behavior.

Although the magnitude of the diffusion coefficient is as expected, the low activation energy and the low D_0 for diffusion of cesium in single-crystal tantalum are surprising from a theoretical point of view. Low values of these parameters are more typical of polycrystalline samples where large-angle grain boundary diffusion is dominant.

B. Weight-Loss Experiments

The weight-loss measurement of cesium permeation through a 0.002-in.-thick polycrystalline wall gives a permeation rate of $0.04 \mu\text{g}/\text{cm}^2\text{-sec}$ ($30 \mu\text{a}/\text{cm}^2$) at 1800° C . (The weight-loss apparatus had a permeation area of 20 cm^2 .) If the wall were 0.010-in. thick (for comparison to other results), the ion permeation rate would be $6 \mu\text{a}/\text{cm}^2\text{-sec}$ at 1800° C . This would neutralize an electron current of only 2.8 ma and is therefore still too small for practical use. It is, however, about 36 times larger than permeation rates derived from the tracer studies on single crystals. This would be expected because the weight-loss apparatus used polycrystalline tantalum, so there should be a contribution from large-angle grain boundary diffusion. However, the permeation activation energy is 4.05 eV (93.4 kcal/mole) compared to a diffusion activation energy of 1.06 eV derived from the tracer studies on single crystals.

It is not expected that the diffusion activation energy would be larger in polycrystalline samples than in single crystals. The permeation activation energy, however, also includes a solubility activation energy.

The permeation rate limiting mechanism is not determined as such from the weight-loss experiments. Possibly, one of the other permeation-limiting mechanisms mentioned in section II might be unexpectedly small and thus be rate limiting, causing the large activation energy.

Oxygen contamination of the tantalum from the vacuum and/or residual oxygen in the metal could be a possible explanation for the high activation energy observed for the weight-loss studies, since the heat of evaporation of tantalum oxide is approximately 5.6 eV at 2000° K.²⁸ However, these processes are ruled out by the before and after weight comparison of the tantalum vessel, which showed no weight change, and by the fact that the residual oxygen content of the metal was too low to account for the large weight change.

Thus, the weight-loss results are not consistent with the tracer studies of diffusion coefficient but do rule out practical use of permeation in thermionic devices.

C. Ion-Current Experiments

The tracer studies in single crystals indicate a permeation rate of 1.06×10^{12} atoms/cm²-sec ($0.17 \mu\text{a/cm}^2$) at 1800° C. In 24 hours this would yield an integrated permeation of 8.7×10^{16} atoms/cm². The weight-loss data would imply an integrated permeation of 4.1×10^{18} atoms/cm². Because a monolayer of ions would be about 9×10^{14} /cm², this total permeation (based on either tracer or weight-loss data) should be sufficient to coat the inner surface of the glass envelope and metal collector with a monolayer of cesium ions and bring the diode-interspace to equilibrium room temperature cesium pressure. Later application of a cold trap to an attached reservoir (which leaves the diode itself at room temperature) will not quickly reduce the cesium pressure, because the 5×10^{14} atoms/cm²-sec room temperature arrival rate to the reservoir would require some time to remove the accumulated cesium. Therefore, although the ion current is too small to be directly measured, it could be observed as a cumulative effect after many hours. However, a leak and diffusion would give the same cumulative effect.

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R. A. Chapman, D. A. Peterman, P. F. Woerner, E. F. Wakefield
Summary Report, January 1963
[Contract Monr-3705 (00)/fm] Proj. No. 099-364

A plasma thermionic converter concept has been proposed which uses cesium permeation through a tantalum emitter to obtain space charge neutralization of electron current from this emitter. The objective of this project was to determine if the permeation rate of cesium through tantalum was sufficiently large for feasibility of the concept. It has been shown that the concept is not feasible because the permeation rate of Cs through tantalum is too small.

Cesium permeation through tantalum has been studied in the temperature range 1400° C to 1800° C with cesium pressures up to 13 mm-Hg. This phenomenon was investigated for potential application as a hollow, ion-dispersing emitter for a plasma thermionic converter. Three methods were used in this study: (1) measurement of ion current from a hollow, polycrystalline tantalum emitter internally connected to a cesium reservoir, (2) measurement of weight-loss from a hollow, polycrystalline tantalum container with a cesium reservoir attached, with both suspended from a microbalance into a radiant furnace, and (3) direct measurement of the diffusion coefficient in single-crystal and polycrystalline tantalum utilizing radioactive Cs¹³⁴.

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From this study we have found: (1) the diffusion coefficient of cesium in single crystal tantalum is $4.9 \times 10^{-10} \text{ cm}^2/\text{sec}$ at 1800°C ; the diffusion activation energy is 1.06 eV and the pre-exponential factor is $2.47 \times 10^{-7} \text{ cm}^2/\text{sec}$; (2) diffusion in polycrystalline samples was irregular and strongly dependent on grain structure; (3) the weight-loss from polycrystalline vessel with walls 0.002-in. thick depends on annealing history but is the order of $0.04 \mu\text{g}/\text{cm}^2 - \text{sec}$ ($30 \mu\text{A}/\text{cm}^2$) at 1800°C with permeation activation energy of 4.05 eV ; and (4) prior observations of ion-current from hollow emitters could be attributed to physical leaks.

This study indicates that the permeation rate through a 0.010-in. -thick tantalum emitter at 1800°C is much too small to neutralize 5 amps/cm^2 of electron current. For single-crystal tantalum the neutralized electron current would be no higher than $0.85 \text{ mA}/\text{cm}^2$ (using tracer data and assuming a maximum cesium concentration of 0.1 at. \% in tantalum) and for polycrystalline tantalum $3.0 \text{ mA}/\text{cm}^2$ of electron current (from weight-loss data). Thus, the permeation currents are too small for practical application. This permeation could have a long-term effect, producing a cesium loss from the diode in designs having thin, hot tantalum separating the diode-inter-space from vacuum (space applications).

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